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JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in *italics* represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
<i>Abh. Böhm. Akad.</i> . . .	Abhandlungen der Böhmischen Akademie.
<i>Abh. Deut. Naturwiss. Med. Ver. Böhmen.</i> . . .	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
<i>Acad. Sci. Fennicae</i> . . .	Acta Societatis Scientiarum Fennicae.
<i>Agric. Bull. F. M. S.</i> . . .	Agricultural Bulletin of the Federated Malay States.
<i>Agric. Exp. Stat. Univ. Wisconsin Res. Bull.</i> . . .	Agricultural Experimental Station, University of Wisconsin, Research Bulletin.
<i>Agric. Gaz. S. Russia.</i> . . .	Agricultural Gazette of Southern Russia.
<i>Agric. J. India</i> . . .	Agricultural Journal of India.
<i>Agric. Ledger</i> . . .	Agricultural Ledger.
<i>Agric. Res. Inst., Pusa Rep. (Bull.)</i> . . .	Agricultural Research Institute, Pusa, Report and Bulletins.
<i>Agric. and Sylvic.</i> . . .	Agriculture and Sylviculture (Petrograd).
<i>Allgem. Brau.-Hopf. Zeit.</i> . . .	Allgemeine Brau- und Hopfen-Zeitung.
<i>Allgem. Gerber-Zeit.</i> . . .	Allgemeine Gerber-Zeitung.
<i>Allgem. Z. Bierbrau. u. Malzfabr.</i> . . .	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
<i>Amat. Fotog.</i> . . .	Amator Fotografen.
<i>Amer. Brewers' J.</i> . . .	American Brewers' Journal.
<i>Amer. Brewers' Rev.</i> . . .	American Brewers' Review.
<i>Amer. J. Bot.</i> . . .	American Journal of Botany.
<i>Amer. J. Dis. Children</i> . . .	American Journal of Diseases of Children.
<i>Amer. J. Pharm.</i> . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . .	American Journal of Physiology.
<i>Amer. J. Publ. Health</i> . . .	American Journal of Public Health.
<i>*Amer. J. Sci.</i> . . .	American Journal of Science.
<i>Amer. Mach.</i> . . .	American Machinist.
<i>Amer. Min.</i> . . .	American Mineralogist.
<i>Amer. Perf.</i> . . .	American Perfumer.
<i>Amer. Phot.</i> . . .	American Photography.
<i>Anal. Fis. Quim.</i> . . .	Anales de la Sociedad Española Física y Química.
<i>Anal. Soc. Quim. Argentina</i> . . .	Anales de la Sociedad Química Argentina.
<i>Analyst</i> . . .	Analyst.
<i>Annalen</i> . . .	Justus Liebig's
<i>Ann. Bot.</i> . . .	Annals of Bot.
<i>Ann. di Bot.</i> . . .	Annali di Bot.
<i>Ann. Chim.</i> . . .	Annales de Chim.
<i>Ann. Chim. Analyt.</i> . . .	Annales de Chim. Analyt.
<i>Annali Chim. Appl.</i> . . .	Annali di Chim. Appl.
<i>Ann. Ecole Agric. Montpellier</i> . . .	Annales de l'Ecole Nationale d'Agriculture de Montpellier.
<i>Ann. Falsif.</i> . . .	Annales des Falsifications.
<i>Ann. Geol. Min. Russie</i> . . .	Annuaire de la Géologie et de la Minéralogie de Russie.
<i>Ann. hyg. pub. med. legale.</i> . . .	Annales d'hygiène publique et de médecine légale.
<i>Ann. Inst. Mines, Petrograd</i> . . .	Annales de l'Institut des Mines, Petrograd.
<i>Ann. Inst. Pasteur</i> . . .	Annales de l'Institut Pasteur.
<i>Ann. Inst. Polyt., Petrograd</i> . . .	Annales de l'Institut Polytechnique, Petrograd.
<i>Ann. Physik</i> . . .	Annalen der Physik.
<i>Ann. Physique</i> . . .	Annales de Physique.
<i>Ann. R. Staz. Chim. Agrar. Sperim.</i> . . .	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
<i>Ann. sci. Univ. Jassy</i> . . .	Annales scientifiques de l'Université de Jassy.

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IARI

ABBREVIATED TITLE.	JOURNAL.
<i>Ann. Soc. Geol. Belg. : Publ. rel. au Congo Belge</i>	Annales de la Société géologique de Belgique : Publications relatives au Congo Belge.
<i>Apoth. Zeit.</i>	Apotheker-Zeitung.
<i>App. Sci.</i>	Applied Science.
<i>Arb. Gebiet. Physik, Math. Chem.</i>	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
<i>Arb. Gesundh. Amt.</i>	Arbeiten aus dem Gesundheitsamte.
<i>Arch. Anat. Physiol.</i>	Archiv für Anatomie und Physiologie.
<i>Arch. Chem. Mikros.</i>	Archiv Chemie und Mikroskopie.
<i>Arch. Entw.-mech. Org.</i>	Archiv für Entwicklungsmechanik der Organismen.
<i>Arch. expt. Path. Pharm.</i>	Archiv für experimentelle Pathologie und Pharmakologie.
<i>Arch. farm. sper. sci. aff.</i>	Archivio di farmacologia sperimentale e scienze affini
<i>Arch. Fisiol.</i>	Archivio di Fisiologia.
<i>Arch. Hyg.</i>	Archiv für Hygiene.
<i>Arch. Int. Med.</i>	The Archives of Internal Medicine.
<i>Arch. ital. Biol.</i>	Archives italiennes de Biologie.
<i>Arch. Med. Pharm. milit.</i>	Archives de Médecine et de Pharmacie militaires.
<i>Arch. Néerland.</i>	Archives Néerlandaises de sciences exactes et naturelles.
<i>Arch. Néerland. physiol.</i>	Archives Néerlandaises de physiologie de l'homme et des animaux.
<i>*Arch. Pharm.</i>	Archiv der Pharmazie.
<i>Arch. physikal. Chem. Glas. Keram.</i>	Archiv für die physikalische Chemie der Gläser und der Keramischen Massen.
<i>Arch. Sci. biol. Petrograd.</i>	Archives des Sciences biologiques, Petrograd.
<i>Arch. Sci. phys. nat.</i>	Archives des Sciences physiques et naturelles.
<i>Arch. Suikerind. Ned. Indie</i>	Archief voor de Suikerindustrie in Nederlandsch Indië.
<i>Arkiv. Kem. Min. Geol.</i>	Arkiv. för Kemi, Mineralogi och Geologi.
<i>Arm. Beton</i>	Armierter Beton.
<i>*Atti R. Accad. Lincei</i>	Atti della Reale Accademia dei Lincei.
<i>Atti R. Accad. Sci. Torino</i>	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Ist. Veneto Sci.</i>	Atti del Istituto Veneto di Scienze, Lettere ed Arti.
<i>Aust. Pharm. Notes</i>	Australian Pharmaceutical Notes and News.
<i>Beitr. Min. Japan</i>	Beiträge zur Mineralogie von Japan.
<i>Berg. Hüttenm. Rundsch.</i>	Berg- und Hüttenmannisches Rundschau.
<i>*Ber.</i>	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i>	Berichte der Deutschen botanischen Gesellschaft.
<i>Ber. Deuts. pharm. Ges.</i>	Berichte der Deutschen pharmazeutischen Gesellschaft.
<i>Ber. Deut. physikal. Ges.</i>	Berichte der Deutschen physikalischen Gesellschaft.
<i>Ber. K. Sächs. Ges. Wiss.</i>	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
<i>Ber. Oberhess. Ges. Natur. Heilkunde.</i>	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Gießen.
<i>Ber. Ohara Inst. landw. Forsch.</i>	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
<i>Berlin. Klin. Woch.</i>	Berliner Klinische Wochenschrift.
<i>*Bied. Zentr.</i>	Biedermann's Zentralblatt für Agrikulturchemie und rationalen Landwirtschafts-Betrieb.
<i>Biochem. Bull.</i>	Biochemical Bulletin.
<i>*Biochem. J.</i>	Biochemical Journal.
<i>*Biochem. Zeitsch.</i>	Biochemische Zeitschrift.
<i>Blätter Zucker.</i>	Blätter für Zuckerrübenbau.
<i>Bd. of Trade J.</i>	Board of Trade Journal.
<i>Bol. Acad. Nac. Ciencias, Córdoba.</i>	Boletín de la Academia Nacional des Ciencias, Córdoba.
<i>Boll. Chim. farm.</i>	Bollettino Chimico farmaceutico.
<i>Boll. Soc. Geol. Ital.</i>	Bollettino della Società Geologica Italiana.
<i>Boll. Soc. Med.-Chirurg.</i>	Bollettino della Società Medico-Chirurgica, Padova.

ABBREVIATED TITLE.	JOURNAL.
<i>Bot. Centr.</i>	Botanisches Centralblatt.
<i>Bot. Gaz.</i>	Botanical Gazette.
<i>Brass. Malt.</i>	Brasserie et Malterie.
<i>Brau- u. Malzind.</i>	Brau- u. Malzindustrie.
<i>Braunkohle</i>	Braunkohle.
<i>Brewers' J.</i>	Brewers' Journal.
<i>Brit. and Col. Pharm.</i>	British and Colonial Pharmacist.
<i>Brit. J. Phot.</i>	British Journal of Photography.
<i>Brit. Med. J.</i>	British Medical Journal.
<i>Brit. Pat.</i>	British Patent.
<i>Buletinul Chim.</i>	Buletinul Chimie.
<i>Bul. Soc. Chim. România.</i>	Buletinul Societății de Chimie din România.
<i>Bul. Soc. Romane Stiin.</i>	Buletinul Societății Romane de Științe.
<i>Bull. Acad. roy. Belg.</i>	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Acad. Sci. Cracow</i>	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Acad. Sci. Petrograd.</i>	Bulletin de l'Académie Impériale des Sciences de Petrograd.
<i>Bull. Acad. Sci. Roumaine</i>	Bulletin de la Section Scientifique de l'Académie Roumaine.
<i>Bull. Agric. Intell.</i>	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
<i>Bull. Assoc. Chim. Sucr.</i>	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
<i>Bull. Bureau of Standards (U.S.A.).</i>	Bulletin of the Bureau of Standards (U.S.A.).
<i>Bull. Com. Géol. Finla. ic.</i>	Bulletin de la Commission Géologique de Finlande.
<i>Bull. Dept. Agric. Ceylon.</i>	Bulletin of the Department of Agriculture, Ceylon.
<i>Bull. Dept. Agric. Trinidad</i>	Bulletin of the Department of Agriculture, Trinidad.
<i>Bull. Forest Exp. Stat. Meguro.</i>	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
<i>Bull. gén. Thérap.</i>	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
<i>Bull. Geol. Inst. Univ. Upsala.</i>	Bulletin of the Geological Institution of the University of Upsala.
<i>Bull. Geol. Soc. Amer.</i>	Bulletin of the Geological Society of America.
<i>Bull. Geol. Survey, U. S. A.</i>	Bulletin of the U.S. Geological Survey.
<i>Bull. Geol. Survey, West Australia.</i>	Bulletin of the Geological Survey, West Australia.
<i>Bull. Imp. Centr. Agric. Exp. Stat. Japan.</i>	Bulletin of the Imperial Central Agricultural Experimental Station of Japan.
<i>Bull. Imp. Inst.</i>	Imperial Institute Bulletin.
<i>Bull. Johns Hopkins Hospital</i>	Bulletin of Johns Hopkins Hospital.
<i>Bull. Ranade Indus. Econ. Inst. Poona.</i>	Bulletin of the Ranade Industrial and Economic Institute, Poona.
<i>Bull. School Mines and Met., Univ. Missouri</i>	Bulletin of the School of Mines and Metallurgy, University of Missouri.
<i>Bull. Sci. Pharmacol.</i>	Bulletin des Sciences Pharmacologiques.
<i>*Bull. Soc. chim.</i>	Bulletin de la Société chimique de France.
<i>*Bull. Soc. chim. Belg.</i>	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. chim. biol.</i>	Bulletin de la Société de chimie biologique.
<i>Bull. Soc. chim. Maurice</i>	Bulletin de la Société chimique de Maurice.
<i>Bull. Soc. d'Encour.</i>	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
<i>Bull. Soc. franç. Min.</i>	Bulletin de la Société française de Minéralogie.
<i>Bull. Soc. Franç. Phot.</i>	Bulletin de la Société Française de Photographie.
<i>Bull. Soc. Ind. Mulhouse</i>	Bulletin de la Société Industrielle de Mulhouse.
<i>Bull. Soc. Ind. Nord.</i>	Bulletin de la Société Industrielle du Nord de la France.

ABBREVIATED TITLE.	JOURNAL.
Bull. Soc. Ind. Rouen .	Bulletin de la Société Industrielle de Rouen.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop. Res. Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J.	Cairo Scientific Journal.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
Canadian Med. Assoc. J. .	Canadian Medical Association Journal.
Canadian Mining J. . . .	Canadian Mining Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cement	Cement.
*Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Kunstdüngerind. . .	Centralblatt für Kunstdüngerindustrie.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Centr. Zuckerind.	Centralblatt für Zuckerindustrie.
Céramique	Céramique.
Ch. of Comm. J.	Chamber of Commerce Journal.
Chemik Polski	Chemik Polski.
Chem. App.	Chemische Apparatur.
Chem. Eng.	Chemical Engineer.
Chem. Erde	Chemie der Erde.
Chem. Ind.	Chemische Industrie.
*Chem. News	Chemical News.
Chem. Trade J.	Chemical Trade Journal.
Chem. Umschau Fett-Ind.	Chemische Umschau über die Fett- und Harz-Industrie.
*Chem. Weekblad	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zeitsch.	Chemische Zeitschrift.
*Chem. Zentr.	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
*Chim. et Ind.	Chimie et Industrie.
Collegium	Collegium.
*Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. l'Acad. d'Agric.	Comptes rendus des Séances de l'Académie d'Agriculture de France.
Compt. rend. Soc. Biol. . .	Comptes rendus hebdomadaires des Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Carlsberg.
D. R.-P.	Deutscher Reichs-Patent.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Derm. Woch.	Dermatologische Wochenschrift.
Deut. Essigind.	Deutsche Essigindustrie.
Deut. Mechan. Zeit. . . .	Deutsche Mechaniker Zeitung.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Parfum. Zeit. . . .	Deutsche Parfumerie Zeitung.
Deuts. Zuckerind.	Deutsche Zuckerindustrie.
Econ. Geol.	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Electrician	Electrician.
Elektrochem. Zeits. . . .	Elektrochemische Zeitschrift.
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News	Engineering News.
Eng. Rec.	Engineering Record.
Engrais	L'Engrais.

ABBREVIATED TITLE.	JOURNAL.
Exper. Stat. Rec. . . .	Experimental Station Record.
Fachl. Mitt. Öst. Tabak. . .	Fachliche Mitteilungen der Österreichische Tabakregie.
Farber-Zeit. . . .	Färber-Zeitung.
Farben-Zeit. . . .	Farben-Zeitung.
Farm	The Farm (Russia).
Fermentforsch. . . .	Fermentforschung.
Ferrum	Ferrum.
Feuerungstechnik	Feuerungstechnik.
Flora	Flora.
Földtani Közlöny	Földtani Közlöny.
Fr. Pat. . . .	French Patent.
Fühlings Landw. Zeit. . .	Fühlings Landwirtschaftliche Zeitung.
Gas	Het Gas.
Gas J. . . .	Gas Journal.
Gas Rec. . . .	Gas Record.
*Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh. . . .	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag. . . .	Geological Magazine.
Gerber	Gerber.
Gesundheitsing. . . .	Gesundheitsingenieur.
Gornosaw. Djelo	Gornosawodskoje Djelo.
Gummi-Zeit. . . .	Gummi-Zeitung.
Handl. Vijft. Nat. . . .	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull. . . .	Hawaii Agricultural Experiment Station Bulletins.
Heurt. . . .	Heart.
Helv. Chim. Acta	Helvetica Chimica Acta.
Hess. Landw. Zeits. . . .	Hessische Landwirtschaftliche Zeitschrift.
Hyg. Rundsch. . . .	Hygienische Rundschau.
Indian Forest Bull. . . .	Indian Forest Bulletin.
Indian J. Med. Res. . . .	Indian Journal of Medical Research.
India-rubber J. . . .	India-rubber Journal.
Ingenieur	De Ingenieur.
Int. Mitt. Bodenk. . . .	Internationale Mitteilungen für Bodenkunde.
Int. Sugar J. . . .	International Sugar Journal.
Int. Z. Metallog. . . .	Internationale Zeitschrift für Metallographie.
Int. Zeitsch. phys.-chem. Biol. . . .	Internationale Zeitschrift für physikalisch-chemische Biologie.
Iron Steel Inst. Carnegie Schol. Mem. . . .	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Jahrb. K. K. Geol. Reichsanst. . . .	Jahrbuch der K. K. geologischen Reichsanstalt.
Jahrb. Min. . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd. . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv. Elek- tronik. . . .	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot. . . .	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur. . . .	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Jernk. Ann. . . .	Jernkontorets Annaler.
J. d'Agric. prat. . . .	Journal d'Agriculture Pratique.
*J. Agric. Res. . . .	Journal of Agricultural Research.
*J. Agric. Sci. . . .	Journal of Agricultural Science.
J. d'Agric. Trop. . . .	Journal d'Agriculture Tropique.
J. Agric. Victoria	Journal of Agriculture, Victoria.
*J. Amer. Chem. Soc. . . .	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc. . . .	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc. . . .	Journal of the American Medical Association.
J. Amer. Pharm. Assoc. . . .	Journal of the American Pharmaceutical Association.

ABBREVIATED TITLE.	JOURNAL.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
* <i>J. Biol. Chem.</i> . . .	Journal of Biological Chemistry, New York.
J. Board Agric. . . .	Journal of the Board of Agriculture.
J. Canad. Min. Inst. . . .	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo . . .	See Kōgyō- Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chim. physique</i> . . .	Journal de Chimie physique.
J. Coll. Agric. Sapporo . . .	Journal of the College of Agriculture, Sapporo, Japan.
J. Coll. Agric. Tohoku . . .	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
J. Coll. Agric. Tokyo . . .	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
J. Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
* <i>J. Coll. Sci. Tokyo</i> . . .	Journal of the College of Science, Imperial University of Tokyo.
<i>J. Exp. Med.</i> . . .	Journal of Experimental Medicine.
J. Franklin Inst. . . .	Journal of the Franklin Institute.
J. Gasbeleucht. . . .	Journal für Gasbeleuchtung und Wasserversorgung.
<i>J. gen. Physiol.</i> . . .	Journal of general Physiology.
<i>J. Genetics</i> . . .	Journal of Genetics.
<i>J. Geol.</i> . . .	Journal of Geology.
<i>J. Geol. Soc. Tokyo</i> . . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
<i>J. Hygiene</i> . . .	Journal of Hygiene.
J. Imp. Gas Assoc. Tokyo	Journal of the Imperial Gas Association of Tokyo.
J. Ind. Eng. Chem. . . .	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing . . .	Journal of the Institute of Brewing.
J. Inst. Petroleum Tech. . . .	Journal of the Institute of Petroleum Technologists.
J. Inst. Sanit. Eng. . . .	Journal of the Institute of Sanitary Engineers.
J. Landw. . . .	Journal für Landwirtschaft.
J. Manchester School Tech.	Journal of the Manchester School of Technology.
<i>J. Marine Biol. Assoc. U.K.</i>	Journal of the Marine Biological Association of the United Kingdom.
<i>J. Med. Res.</i> . . .	Journal of Medical Research.
<i>J. Path. Bact.</i> . . .	Journal of Pathology and Bacteriology.
J. Pharm. Chim. . . .	Journal de Pharmacie et de Chimie.
<i>J. Pharm. Expt. Ther.</i> . . .	Journal of Pharmacology and Experimental Therapeutics.
* <i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. Physiol. Path. gén.</i> . . .	Journal de Physiologie et de Pathologie générale.
* <i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Proc. Asiatic Soc. Bengal.</i>	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Agric. Soc. . . .	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps . . .	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc. . . .	Journal of the Royal Horticultural Society.
<i>J. Roy. Soc. New South Wales.</i>	Journal and Proceedings of the Royal Society of New South Wales.
<i>J. Roy. Soc. West Australia</i>	Journal of the Royal Society of West Australia.
* <i>J. Russ. Phys. Chem. Soc.</i>	Journal of the Physical and Chemical Society of Russia.
<i>J. Scot. Met. Soc.</i> . . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . .	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col. . . .	Journal of the Society of Dyers and Colourists.
J. Soc. Russe Métall. . . .	Journal de la Société Russe de Métallurgie.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.

ABBREVIATED TITLE.	JOURNAL.
J. Textile Inst.	Journal of the Textile Institute.
J. Usines Gaz	Journal des Usines à Gaz.
<i>J. Washington Acad. Sci.</i>	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
<i>K. Svenska Vet.-Akad. Handl.</i>	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kali	Kali.
Karbid u. Azet.	Karbid und Azetylen.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch.	Keramisch Rundschau.
Kew Bull.	Kew Bulletin.
Kiserlet Közl.	Kiserlet Közlemények.
Klein u. Mittelbrauer	Klein und Mittelbrauer.
Kongl. Landtbr. Handl. Tidskr.	See Bull. Agric. Intell.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
* <i>Kolloid Zeitsch.</i>	Kolloid Zeitschrift.
* <i>Koll. Chem. Beihefte</i>	Kolloid-chemische Beihefte.
<i>Kosmos</i>	Kosmos (Lemberg).
<i>Kühn-Archiv</i>	Kühn-Archiv.
Kunststoffe	Kunststoffe.
<i>Lancet</i>	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev.	Leather Trades Review.
Leather Trades Year Book	Leather Trades Year Book.
Leather World	Leather World.
Ledertech. Rundsch.	Ledertechnische Rundschau.
Leipzig. Monatsch. Textil-Ind.	Leipziger Monatschrift für Textil-Industrie.
<i>Le Radium</i>	Le Radium.
L'Ind. Chimica	L'Industria Chimica.
L'Ind. Chimique	L'Industrie Chimique.
Lilly Sci. Bull.	Lilly Scientific Bulletin.
Local Govt. Bd. Reports	Local Government Board Reports.
Louisiana Bull.	Louisiana Bulletin.
Louisiana Planter	Louisiana Planter.
<i>Lunds. Univ. Årsskr.</i>	Lunds Universitets Års-skrift.
<i>Math. és Termész. Ért.</i>	Mathematikai és Természettudományi Értesítő, Budapest.
Mat. Grasses	Les Matières Grasses.
<i>Medd. K. Vetenskapsakad. Nobel-Inst.</i>	Meddelanden från Kongl.-Vetenskapsakademiens Nobel-Institut.
<i>Medd. on Grönland</i>	Meddelser on Grönland.
<i>Med. Chron.</i>	Medical Chronicle.
<i>Med. Klinik</i>	Medizinische Klinik.
<i>Mem. Acad. Sci. Petrograd.</i>	Mémoires de l'Académie Impériale des Sciences de Petrograd.
<i>Mem. Accad. Lincei</i>	Memorie della Reale Accademia dei Lincei.
<i>Mem. Accad. Sci. Torino</i>	Memorie della Reale Accademia delle Scienze di Torino.
<i>Mem. Coll. Sci. Kyōtō</i>	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Mém. Poudres et Salpêtres.</i>	Mémoriale des Poudres et Salpêtres.

ABBREVIATED TITLE.	JOURNAL.
Mem. Soc. Ing. Civ. . . .	Mémoires de la Société des Ingénieurs Civils de France.
<i>Mem. Soc. Natur. Kiev</i> . . .	Mémoires de la Société des Naturalistes de Kiev.
<i>Mem. Soc. Toscana Sci. Nat.</i>	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz	Metall und Erz.
Met. and Chem. Eng. . . .	Metallurgical and Chemical Engineering.
Metallurgie	Metallurgie.
Metrop. Water Bd. Rep. . .	Metropolitan Water Board Reports.
Milch. Zentr. . . .	Milchwirtschaftliches Zentralblatt.
<i>Min. Mag.</i>	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. and Eng. Rev. . . .	Mining and Engineering Review.
Ministry of Agric. Egypt.	Ministry of Agriculture of Egypt. Technical Science
Tech. Sci. Service	Service.
Mitt. Centralst. wiss.-techn.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen.
Unters.	
Mitt. deut. Landw.-Ges. . .	Mittheilungen der deutschen Landwirthschafts-Gesellschaft.
Mitt. deut. milchwirt. Ver.	Mittheilungen des deutschen milchwirtschaftlichen Vereins.
<i>Mitt. geol. Landesanst.</i> . .	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. k. Materialprüf. . . .	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. k. k. Techn. Versuchsamt	Mittheilungen des k. k. Technischen Versuchsamtes.
<i>Mitt. med. Ges. Tokyo</i> . . .	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
<i>Mitt. Naturforsch. Ges. Halle.</i>	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Molk.-Zeit. . . .	Molkerei-Zeitung.
* <i>Monatsh.</i>	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
<i>Monatsh. Math. Physik</i> . . .	Monatshefte für Mathematik und Physik.
* <i>Mon. Sci.</i>	Moniteur Scientifique.
Montan. Rundsch. . . .	Montanische Rundschau.
<i>Month. Not. Roy. Astr. Soc.</i>	Monthly Notices of the Royal Astronomical Society, London.
<i>Munch. med. Woch.</i>	Münchener medizinische Wochenschrift.
Mycol. Zentr. . . .	Mycologisches Zentralblatt.
<i>Nachr. Ges. Wiss. Göttingen.</i>	Nachrichten von der Königl. Gesellschaft der Wissenschaften zu Göttingen.
<i>Nature</i>	Nature.
<i>Naturwiss.</i>	Die Naturwissenschaften.
<i>Naturw. Reich.</i>	Naturwissenschaftliche Rundschau.
Nephthanoje Djelo	Nephthanoje Djelo.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
<i>Nova Acta Soc. Sci.</i>	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
<i>Nuovo Cim.</i>	Il Nuovo Cimento.
<i>Öfvers. Finska Vet.-Soc.</i>	Öfversigt af Finska Vetenskaps-Societätens Förhandlingar, Helsingfors.
Oelmotor	Der Oelmotor.
Oesterr. Chem.-Zeit. . . .	Oesterreichische Chemiker-Zeitung.
Oesterr. Z. Berg- u. Hüttenw.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen.
Oil and Colour Trades J. . .	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep. .	Oil, Paint, and Drug Reporter.

ABBREVIATED TITLE.	JOURNAL.
<i>Oversigt Danske Vid. Selsk.</i>	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
<i>P.</i>	Proceedings of the Chemical Society.
<i>Pahasapa Quart.</i>	Pahasapa Quarterly.
<i>Paper</i>	Paper.
<i>Paper Maker</i>	Paper Maker.
<i>Paper Making</i>	Paper Making.
<i>Papierfabr.</i>	Papier-Fabrikant.
<i>Papier-Zeit.</i>	Papier-Zeitung.
<i>Perf. and Essent. Oil Rec.</i>	Perfumery and Essential Oil Record.
<i>Per. spis. Sofia</i>	Periodicesko spisanie Sofia.
<i>Petroleum</i>	Petroleum.
<i>Pflüger's Archiv.</i>	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i>	Pharmaceutical Journal.
<i>Pharm. Post.</i>	Pharmazeutische Post.
<i>Pharm. Weekblad</i>	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i>	Pharmazeutische Zeitung.
<i>Pharm. Zentr.-h.</i>	Pharmazeutische Zentralhalle.
<i>Pharmazevt. J.</i>	Pharmazevtizieski Journal.
<i>Phil. Mag.</i>	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i>	Philosophical Transactions of the Royal Society of London.
<i>Philippine J. Sci.</i>	Philippine Journal of Science.
<i>Phot. Ind.</i>	Photographische Industrie.
<i>Phot. J.</i>	Photographic Journal.
<i>Phot. Korr.</i>	Photographische Korrespondenz.
<i>Phot. Rundsch.</i>	Photographische Rundschau.
<i>Physical Rev.</i>	Physical Review.
<i>Physikal. Zeitsch.</i>	Physikalische Zeitschrift.
<i>Porto Rico Exper. Stat. Bull.</i>	Porto Rico Experiment Station Bulletin.
<i>Proc. Amer. Phil. Soc.</i>	Proceedings of the American Philosophical Society.
<i>Proc. Amer. Physiol. Soc.</i>	Proceedings of the American Physiological Society.
<i>*Proc. Amer. Soc. Biol. Chem.</i>	Proceedings of the American Society of Biological Chemists.
<i>Proc. Amer. Soc. Civ. Eng.</i>	Proceedings of the American Society of Civil Engineers.
<i>Proc. Amer. Soc. Testing Materials</i>	Proceedings of American Society for Testing Materials.
<i>Proc. Amer. Wood Preservers' Assoc.</i>	Proceedings of American Wood Preservers' Association.
<i>Proc. Austral. Inst. Min. Eng.</i>	Proceedings of the Australasian Institute of Mining Engineers.
<i>Proc. Brit. Foundrymen's Assoc.</i>	Proceedings of British Foundrymen's Association.
<i>Proc. Camb. Phil. Soc.</i>	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Durham Phil. Soc.</i>	Proceedings of the Durham Philosophical Society.
<i>Proc. Eng. Soc. W. Pa.</i>	Proceedings of the Engineers' Society of Western Pennsylvania.
<i>Proc. Inst. Civ. Eng.</i>	Proceedings of the Institution of Civil Engineers.
<i>Proc. Inst. Mech. Eng.</i>	Proceedings of the Institution of Mechanical Engineers.
<i>Proc. Inst. Min. and Met.</i>	Proceedings of the Institution of Mining and Metallurgy.
<i>*Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Nat. Acad. Sci.</i>	Proceedings of the National Academy of Sciences.
<i>Proc. Nova Scotia Inst. Sci.</i>	Proceedings of the Nova Scotia Institute of Science.
<i>Proc. Phil. Soc. Glasgow</i>	Proceedings of the Glasgow Philosophical Society.
<i>Proc. Physical Soc. London.</i>	Proceedings of the Physical Society of London.

ABBREVIATED TITLE.	JOURNAL.
<i>Proc. Physiol. Soc.</i> . . .	Proceedings of the Physiological Society.
<i>Proc. Roy. Inst.</i> . . .	Proceedings of the Royal Institution of Great Britain.
<i>Proc. Roy. Irish Acad.</i> . . .	Proceedings of the Royal Irish Academy.
* <i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. Edin.</i> . . .	Proceedings of the Royal Society of Edinburgh.
<i>Proc. Roy. Soc. Med.</i> . . .	Proceedings of the Royal Society of Medicine.
<i>Proc. Roy. Soc. Queensland.</i> . . .	Proceedings of the Royal Society of Queensland.
<i>Proc. Roy. Soc. Tasmania.</i> . . .	Proceedings of the Royal Society of Tasmania.
<i>Proc. Soc. Chem. Ind. Victoria.</i> . . .	Proceedings of the Society of Chemical Industry, Victoria.
<i>Proc. Soc. Exp. Biol. Med.</i> . . .	Proceedings of the Society for Experimental Biology and Medicine.
<i>Proc. U.S. Nat. Mus.</i> . . .	Proceedings of the United States National Museum.
<i>Proc. verb. Soc. Toscana Sci. Nat.</i> . . .	Processi verbali Società Toscana di Scienze Naturali.
<i>Quart. J. Exp. Physiol.</i> . . .	Quarterly Journal of Experimental Physiology.
<i>Quart. J. Geol. Soc.</i> . . .	Quarterly Journal of the Geological Society.
<i>Quart. J. Med.</i> . . .	Quarterly Journal of Medicine.
<i>Queensland Agric. J.</i> . . .	Queensland Agricultural Journal.
<i>Radium in Biol. Heilkunde</i> . . .	Radium in Biologie und Heilkunde.
<i>Rec. Australian Mus.</i> . . .	Records of the Australian Museum.
<i>Rec. trav. bot. Néerland.</i> . . .	Recueil des travaux botaniques Néerlandaises.
* <i>Rec. trav. chim.</i> . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. Fis. Mat. Napoli.</i> . . .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
<i>Rend. Ist. Lomb. Sci. Lett.</i> . . .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
<i>Rend. Soc. Chim. Ital.</i> . . .	Rendiconto della Società Chimica Italiana.
<i>Rep. Aust. Assoc. Sci.</i> . . .	Report of the Australian Association for the Advancement of Science.
<i>Rep. Brit. Assoc.</i> . . .	Report of the British Association for the Advancement of Science.
<i>Rep. Pharm.</i> . . .	Repertoire de Pharmacie.
<i>Rev. Viticolt.</i> . . .	Revista Viticolt.
<i>Rev. gén. Bot.</i> . . .	Revue générale de Botanique.
<i>Rev. gén. Chim. pure appl.</i> . . .	Revue générale de Chimie pure et appliquée.
<i>Rev. Gén. Mat. Col.</i> . . .	Revue Générale des Matières Colorantes.
<i>Rev. Mét.</i> . . .	Revue de Métallurgie.
<i>Rev. Real Acad. Ciencias exact. Madrid.</i> . . .	Revista de la Real Academia de Ciencias exactas, Físicas y Naturales de Madrid.
<i>Riv. Min. Crist. Ital.</i> . . .	Rivista di Mineralogia e Cristallografia Italiana.
<i>Russian Mining J.</i> . . .	Russian Mining Journal.
<i>Sbornik Klubu Pri.</i> . . .	Sbornik Klubu Prirodovedceho (Prague).
<i>Schimmel's Rep.</i> . . .	Schimmel's Reports.
<i>Schweiz. Apoth. Zeit.</i> . . .	Schweizerische Apotheker Zeitung.
<i>Schweiz. Woch. Chem. Pharm.</i> . . .	Schweizerische Wochenschrift für Chemie und Pharmacie.
<i>Science</i> . . .	Science.
<i>Scient. Amer.</i> . . .	Scientific American.
* <i>Sci. Ind. Rep. Roure-Bertrand Fils.</i> . . .	Scientific and Industrial Reports of Roure-Bertrand Fils.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rep. Tohoku Imp. Univ.</i> . . .	Science Reports, Tohoku Imperial University.
<i>Sci. Trans. Roy. Dubl. Soc.</i> . . .	Scientific Transactions of the Royal Dublin Society.
<i>Seifenfabr.</i> . . .	Der Seifenfabrikant.
<i>Seifensied. Zeit.</i> . . .	Seifensieder Zeitung.
<i>Selsk. Khoz. Les. Petrograd</i> . . .	Selskoie Khoziaistvo i Lesovodstvo Petrograd.
<i>Shoe and Leather Rep.</i> . . .	Shoe and Leather Reporter.
<i>Silikat-Zeits.</i> . . .	Silikat-Zeitschrift.

ABBREVIATED TITLE.	JOURNAL.
<i>Sitzungsber. Ges. Naturwiss. Marburg.</i>	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
<i>Sitzungsber. Heidelberger Akad. Wis.</i>	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Sitzungsber. K. Akad. München.</i>	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.
<i>Sitzungsber. K. Akad. Wiss. Wien.</i>	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
<i>Sitzungsber. Med. Naturwiss. Ges. Münster.</i>	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
<i>Sitzungsber. Naturforsch. Ges. Petrograd.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
<i>Sitzungsber. Naturforsch. Ges. Rostock.</i>	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
<i>Sitzungsber. phys. med. Ges. Erlangen.</i>	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
<i>Skand. Arch. Physiol.</i>	Skandinavisches Archiv für Physiologie.
<i>Smithsonian Miscell. Coll.</i>	Smithsonian Miscellaneous Collections.
<i>Soil Sci.</i>	Soil Science.
<i>South African J. Sci.</i>	South African Journal of Science.
<i>Spezialmonats. Brau- Malz.</i>	Spezialmonatshefte für Brau- und Malzerei betriebskontrolle.
<i>Sprechsaal.</i>	Sprechsaal.
<i>Stahl u. Eisen.</i>	Stahl und Eisen.
<i>Staz. sper. agr. ital.</i>	Stazioni sperimentali agrarie italiane.
<i>Strahlenther.</i>	Strahlentherapie.
<i>Sucr. Indig.</i>	Sucrerie Indigène.
<i>Süddeut. Apoth. Zeit.</i>	Süddeutsche Apotheker Zeitung.
<i>Suikerind.</i>	De Suikerindustrie.
<i>Suom. Tied. Toim.</i>	Suomalaisen Tiedeakatemian Toimituskia.
<i>Svensk Kem. Tidskr.</i>	Svenska Kemisk Tidskrift.
<i>T.</i>	Transactions of the Chemical Society.
<i>Teknikern</i>	Teknikern.
<i>Tekn. Tidsk.</i>	Teknisk Tidskrift.
<i>Textile Col.</i>	Textile Colourist.
<i>Ther. Gegenw.</i>	Die Therapie der Gegenwart.
<i>Ther. Monatsh.</i>	Therapeutische Monatshefte.
<i>Tidsk. Kemi, Farm., Ter.</i>	Tidskrift Kemi, Farm. og Terape.
<i>Tidsk. Teknikern.</i>	Tidskriften Teknikern.
<i>Times Eng. Suppl.</i>	Times Engineering Supplement.
<i>Tonind.-Zeit.</i>	Tonindustrie-Zeitung.
<i>Trans. Amer. Ceram. Soc.</i>	Transactions of the American Ceramic Society.
<i>Trans. Amer. Electrochem. Soc.</i>	Transactions of the American Electrochemical Society.
<i>Trans. Amer. Foundrymen's Assoc.</i>	Transactions of the American Foundrymen's Association.
<i>Trans. Amer. Inst. Chem. Eng.</i>	Transactions of the American Institute of Chemical Engineers.
<i>Trans. Amer. Inst. Metals.</i>	Transactions of the American Institution of Metals.
<i>Trans. Amer. Inst. Min. Eng.</i>	Transactions of the American Institute of Mining Engineers.
<i>Trans. Engl. Ceram. Soc.</i>	Transactions of the English Ceramic Society.
<i>*Trans. Faraday Soc.</i>	Transactions of the Faraday Society.
<i>Trans. Inst. Metals.</i>	Transactions of the Institute of Metals.
<i>Trans. Iron and Steel Inst.</i>	Transactions of the Iron and Steel Institute.
<i>Tr. N. Eng. Inst. Min. and Met.</i>	Transactions of the North of England Institute of Mining and Metallurgy.
<i>Trans. New Zealand Inst.</i>	Transactions of the New Zealand Institute.
<i>Trans. Nova Scotia Inst. Sci.</i>	Transactions of the Nova Scotia Institute of Science.

ABBREVIATED TITLE.	JOURNAL.
<i>Trans. Path. Soc.</i> . . .	Transactions of the Pathological Society.
<i>Trans. Roy. Irish Acad.</i> . . .	Transactions of the Royal Irish Academy.
<i>Trans. Roy. Soc. Canada</i> . . .	Transactions of the Royal Society of Canada.
<i>Trans. Roy. Soc. Edin.</i> . . .	Transactions of the Royal Society of Edinburgh.
<i>Trans. Surveyors' Inst.</i> . . .	Transactions of the Surveyors' Institute.
<i>Trav. Mus. Geol. Acad. Sci. Petrograd.</i>	Travaux de Musée Géologique près l'Académie Impériale des Sciences de Petrograd.
<i>Trav. Soc. Natur. Petrograd.</i>	Travaux de la Société Impériale des Naturalistes de Petrograd.
<i>Tropenpflanzer</i> . . .	Tropenpflanzer.
<i>Tsch. Min. Mitt.</i> . . .	Tschermak's Mineralogische Mitteilungen.
<i>U.S. Bureau of Mines, Bull. and Tech. Papers.</i>	United States Bureau of Mines, Bulletins and Technical Papers.
<i>U.S. Bureau Plant Ind.</i> . . .	United States Bureau of Plant Industry.
<i>U.S. Comm. Rept.</i> . . .	United States Commerce Reports, Daily Consular and Trade Reports.
<i>U.S. Dept. Agric. Bull.</i> . . .	United States Department of Agriculture Bulletins.
<i>U.S. Hyg. Labor. Bull.</i> . . .	United States Hygienic Laboratory Bulletins.
<i>U.S. Pat.</i> . . .	United States Patent.
<i>Univ. Illinois Bull.</i> . . .	University of Illinois Bulletins.
<i>Utah Agric. Coll. Exper. Stat. Bull.</i>	Utah Agricultural College Experiment Station Bulletins.
<i>Ver. deut. Textilver.</i> . . .	Verein deutscher Textilveredlungsindustrie.
<i>Verh. Geol. Reichsanst. Wien.</i>	Verhandlungen der k. k. geologischen Reichsanstalt in Wien.
<i>Verh. Ges. deut. Naturforsch. Aertze.</i>	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Verh. Naturhist. med. Ver. Heidelberg.</i>	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
<i>Verh. Naturhist. Rheinl.</i> . . .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
<i>Verh. Physiol. Ges. Berlin</i> . . .	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
<i>Verh. Schweiz. Nat. Ges.</i> . . .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
<i>Verslag Landb.</i> . . .	Verslag Landbouwkund Onderzoek Ryklandbouwproefstat.
<i>Vet. Rec.</i> . . .	Veterinary Record.
<i>Vict. Mem. Mus. Geol. Survey, Canada.</i>	Victoria Memorial Museum Geological Survey of Canada, Bulletin.
<i>Videnskab. Skrifter</i> . . .	Skrifter udgivne af Videnskabselskabet i Kristiania.
<i>Wasser u. Gas</i> . . .	Wasser und Gas.
<i>West Ind. Agric. News</i> . . .	West Indian Agricultural News.
<i>West Ind. Bull.</i> . . .	West Indian Bulletin.
<i>Westnik Sacch. Prom.</i> . . .	Westnik Saccharnoi Promyschlenosti.
<i>Wiener Klin. Woch.</i> . . .	Wiener Klinische Wochenschrift.
<i>Wiss. Abhandl. Physikal.-Tech. Reichsanst.</i>	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
<i>Wochbl. Papierfabr.</i> . . .	Wochenblatt für Papierfabrikation.
<i>Woch. f. Brau.</i> . . .	Wochenschrift für Brauerei.
<i>Yakugakuzashi</i> . . .	Yakugakuzashi.
<i>Zeitsch. allg. Physiol.</i> . . .	Zeitschrift für allgemeine Physiologie.
<i>*Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Z. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>*Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische und allgemeine Chemie.
<i>Zeitsch. Biol.</i> . . .	Zeitschrift für Biologie.
<i>Zeitsch. deut. Geol. Ges.</i>	Zeitschrift der deutschen Geologischen Gesellschaft.
<i>*Zeitsch. Elektrochem.</i>	Zeitschrift für Elektrochemie.
<i>Zeitsch. exp. Path. Ther.</i>	Zeitschrift für experimentelle Pathologie und Therapie.
<i>Z. Farben-Ind.</i> . . .	Zeitschrift für Farben-Industrie.

ABBREVIATED TITLE.	JOURNAL.
Z. Forst- u. Jagdwesen . . .	Zeitschrift für Forst- und Jagdwesen.
Z. Gärungsphysiol. . . .	Zeitschrift für Gärungsphysiologie.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
<i>Zeitsch. ges. exp. Med.</i> . .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Getreidew. . . .	Zeitschrift für das gesamte Getreidewesen.
Z. ges. Schiess- u. Sprengstoffw. . . .	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
<i>Zeitsch. Hyg.</i>	Zeitschrift für Hygiene und Infektionskrankheiten.
<i>Zeitsch. Immunit.</i>	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
<i>Zeitsch. Instrument.</i> . . .	Zeitschrift für Instrumentenkunde.
Z. Kali	Zeitschrift für Kali.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie
Z. landw. Versuchsw. Oesterr.	Zeitschrift für das landwirtschaftlichen Versuchswesen in Oesterreich.
Z. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
* <i>Zeitsch. physikal. Chem.</i> . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Zeitsch. physikal. Chem. Unterr.</i>	Zeitschrift für den physikalischen und Chemischen Unterricht.
<i>Zeitsch. physiol. Chem.</i> . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. prakt. Geol.</i> . . .	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm. . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. . .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Mikrosk.</i> . . .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
* <i>Zeitsch. wiss. Photochem.</i> . .	Zeitschrift für wissenschaftliche Photographie, Photo-physik und Photochemie.
Z. Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Addition of Hydrogen Bromide to Allyl Bromide. A. F. HOLLEMAN and B. F. H. J. MATTHES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 90—91).—In bright light, hydrogen bromide is absorbed by allyl bromide with the almost quantitative formation of trimethylene bromide, b. p. $167.1^{\circ}/760$ mm.; in the dark, on the other hand, absorption proceeds much more slowly and, whilst trimethylene bromide is the main product, considerable amounts of propylene bromide are also formed. H. W.

Monohydrochloride of Isoprene. OSSIAN ASCHAN (*Ber.*, 1918, **51**, 1303—1307).—Isoprene, which had been prepared from commercial *d*-limonene by means of the isoprene lamp and kept for four years at $4-8^{\circ}$, was fractionated and the portion, b. p. $34-35.5^{\circ}$, D_4^{20} 0.6765, was mixed with 6% of dry ether, cooled in a mixture of snow and sodium chloride, and treated with hydrogen chloride. The product, after being washed with water and dried, was fractionated. The first three fractions, b. p. $65-90^{\circ}$, were treated again in the same way. The fraction, b. p. $107-110^{\circ}$, contains *isoprene monohydrochloride*, C_5H_9Cl , b. p. 109° , D_4^{20} 0.9335, which has an odour resembling that of allyl chloride, combines with hydrogen chloride to form isoprene dihydrochloride (Bouchardat's dichloroisopentane), b. p. $145-146^{\circ}$, D_4^{20} 1.0654, and reacts with bromine in cold chloroform to form a yellow, viscous oil, $C_5H_9ClBr_2$, which cannot be distilled without decomposition.

The isoprene monohydrochloride, b. p. 85—91°, D 0.868, described by Bouchardat in 1879, was almost certainly *tert.*-isomyl chloride. Isoprene prepared from *d*-limonene as above contains β -methyl- Δ^{β} -butylene.

C. S.

Optically Active Propylene Glycol and Optically Active β -Hydroxybutyric Acid. EMIL ABDERHALDEN and EGON LICHWALD (*Ber.*, 1918, 51, 1312—1322).—The specific rotations of the optically active fats previously prepared (A., 1914, i, 801) are unexpectedly small, and active propylene glycol has therefore been prepared in the hope that from it will be obtained more suitable substrates for the study of ferment action.

The desired glycol cannot be isolated from the mixture obtained by the action of nitrous acid on optically active propylenediamine.

Attempts to resolve β -bromo-*n*-propylamine by tartaric, bromocamphorsulphonic, or bromosuccinic acid, formyl-leucine, or similar compounds failed, uncrystallisable syrups being obtained; the resolution of β -chloro-*n*-propylamine, however, is readily effected. A solution of allylamine hydrochloride is saturated at 0° with hydrogen chloride and heated in a sealed tube at 110—120° for five to six hours, the resulting β -chloro-*n*-propylamine is isolated and treated in ether-alcohol solution with *d*-tartaric acid (1 mol.); the precipitate, after being recrystallised ten times from hot water, yields a *d*-tartrate, m. p. 109.5°, $[\alpha]_D^{18} + 36.72^\circ$ in water, from which *d*- β -chloro-*n*-propylamine hydrochloride, $C_3H_9NCl_2$, m. p. 179.5°, $[\alpha]_D^{18} + 34.80^\circ$ in water, is prepared. An aqueous solution of the *d*-tartrate at about 10° is converted by sodium nitrite into *d*- β -chloro- α -propanol, b. p. 40—41°/15 mm., $[\alpha]_D^{18} + 9.26^\circ$. Since the latter could not be obtained quite pure it was added to aqueous potassium hydroxide at 50—70°, and thus converted into *d*-propylene oxide, b. p. 36.5—38°, $[\alpha]_D^{18} + 12.72^\circ$, which has been prepared by Le Bel in a very impure state by fermentation. *d*-Propylene oxide is extensively racemised by water, and on this account must be removed by distillation as rapidly as possible from the aqueous alkali employed in its preparation (above). When added slowly to well-cooled, anhydrous formic acid, it is converted into the formate of propylene glycol, which is readily hydrolysed by 15% hydrochloric acid, yielding *d*-propylene glycol, b. p. 95°/15 mm., $[\alpha]_D^{18} + 13.71^\circ$ in water. The *d*-glycol reacts with butyryl chloride in chloroform solution to form *d*-propylene glycol dibutyryl, $C_{11}H_{20}O_4$, b. p. 95—105°/15 mm., $\alpha + 2.05^\circ$ in 1-dcm. tube.

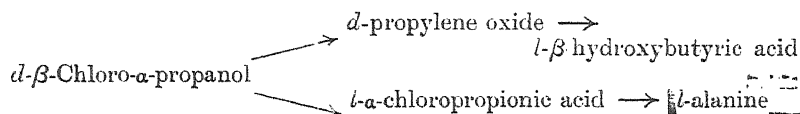
The following *l*-compounds are described: *l*- β -chloro-*n*-propylamine hydrochloride, $[\alpha]_D^{18} - 17.07^\circ$ in water; *l*- β -chloro- α -propanol, $[\alpha]_D^{18} - 2.92^\circ$; *l*-propylene oxide, $[\alpha]_D^{18} - 8.26^\circ$; *l*-propylene glycol, $[\alpha]_D^{18} - 8.97^\circ$ in water.

A synthesis of the optically active, biologically important β -hydroxybutyric acid has been effected and its configuration determined. The addition of hydrogen cyanide to *d*-propylene oxide does not lead to a satisfactory result. *d*-Propylene oxide was therefore converted by cold hydrobromic acid into *l*- β -bromoisopropyl alcohol,

$\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$, b. p. $45-50^\circ/15\text{ mm.}$, $\alpha - 2.05^\circ$ in 1-cm. tube, which reacts readily with potassium cyanide in boiling alcohol to give *l*- β -hydroxybutyronitrile, b. p. $99-100^\circ/15\text{ mm.}$, $[\alpha]_D^{25} - 10.03^\circ$ in water. The last substance is hydrolysed by hot concentrated hydrochloric acid, and yields *l*- β -hydroxybutyric acid, the sodium salt of which has $[\alpha]_D^{25} - 13.28^\circ$ in water.

d- β -Chloro- α -propanol is oxidised by ammonium dichromate and dilute sulphuric acid at the ordinary temperature, and yields *l*- α -chloropropionic acid, which is converted into *l*-alanine by aqueous ammonia.

The preceding configurative relations are shown thus:

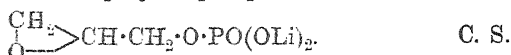


C. S.

Synthesis of Optically Active Glycerophosphoric Acid.

EMIL ABDERHALDEN and EGON EICHWALD (*Ber.*, 1918, 51, 1308—1312).—Since the naturally occurring glycerophosphoric acid is optically active (Willstätter and Lüdecke, *A.*, 1904, i, 1067), one of the first steps in the synthesis of a phosphatide must be the synthesis of glycerophosphoric acid in the optically active form. The authors, employing the optically active halogenhydrins and epihydrins previously prepared by them (*A.*, 1914, i, 801), obtained unsatisfactory results when they attempted to add phosphoric acid to *l*-epihydrin alcohol, epichlorohydrin, or epibromohydrin, and unsuccessful results when they attempted to esterify monochlorohydrin or monobromohydrin with anhydrous phosphoric acid, but achieved success by using Fischer's pyridine-phosphoryl chloride method. Phosphoryl chloride is added slowly to a solution of *d*- α -bromohydrin in dry pyridine, the temperature being kept below -10° ; ice-water is added after one to two hours, the solution is shaken with sufficient silver to remove the chlorine (an excess must be avoided), filtered, treated with hydrogen sulphide, again filtered, and evaporated in a vacuum to remove the hydrogen sulphide and a portion of the pyridine. Barium hydroxide in excess is added, the mixture is diluted, and then concentrated in a vacuum to remove the remainder of the pyridine; the barium in the filtered solution is exactly precipitated with sulphuric acid, and after filtering again the filtrate is without delay treated with 10% lithium hydroxide solution, after twenty-four hours evaporated to a small volume in a vacuum, heated at 80° for one hour, cooled, neutralised with hydrobromic acid, and evaporated in a vacuum until crystals begin to appear; these are redissolved by adding a few c.c. of water, and the filtered solution is treated with alcohol. The precipitate is dissolved in water and precipitated by alcohol, and after a repetition of this treatment is free from lithium bromide. The product is

nearly pure *lithium d-glycerophosphate*, $C_6H_7O_8PLi_2$, $[\alpha]_D^{18} + 3.51^\circ$ in aqueous solution. *Lithium l-glycerophosphate* was also prepared, having $[\alpha]_D^{18} - 3.02^\circ$. By using alcoholic instead of aqueous lithium hydroxide, a glycerophosphate having $[\alpha]_D^{18} + 6.26^\circ$ was obtained, but the higher value may be due to a partial conversion of the glycerophosphate into the epihydrinphosphate,



Preparation of Ethyl Acetate from Acetaldehyde.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 308043; from *Chem. Zentr.*, 1918, ii, 693).—The process depends on the use of a solution of aluminium ethoxide, $\text{Al}(\text{OEt})_3$, which contains at the most only traces of halogen compounds, in an organic solvent of high boiling point, such as solvent naphtha. With such solutions, which allow the most favourable temperature to be readily maintained, the yield of practically pure ethyl acetate exceeds 85% of that theoretically possible; at the same time, the duration of the action is considerably decreased, and the consumption of aluminium ethoxide is reduced to 3–5% of the acetaldehyde. H. W.

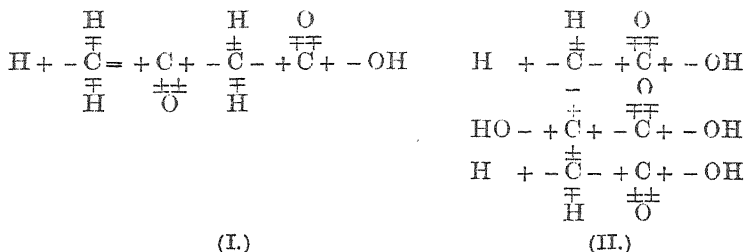
The Velocity of Hydration of the Anhydrides of some Fatty Acids. P. E. VERKADE (*Rec. trav. chim.*, 1918, 37, 315–354).—A theoretical discussion of work already published (compare A., 1914, ii, 256; 1916, ii, 234, 607), in which the author shows that the process of hydration is much more complicated than is shown by the equation $(\text{R} \cdot \text{CO})_2\text{O} + \text{H}_2\text{O} = 2\text{R} \cdot \text{CO}_2\text{H}$. W. G.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. II. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1918, 40, 1674–1707).—A continuation of the theoretical discussion of the subject (compare A., 1918, i, 249). The relationship between the configuration of unsaturated acids and their physical properties (density, m. p., b. p., viscosity, optical activity, magnetic rotation) is examined, and the connexion between configuration and chemical properties (addition, stereomutation, catalysis, esterification) discussed. H. W.

Determination of the Configuration of *cis-trans*-Isomeric Substances. J. BÖSEKEN and CHR. VAN LOON (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 21, 80–89).—A theoretical paper, in which the methods of determining the configuration of *cis-trans* isomerides are critically discussed and their applicability to various types of compounds considered. H. W.

Electronic Constitutions of Acetoacetic and Citric Acids and some of their Derivatives. MILTON TH. HANKE and KARL K. KOESSLER (*J. Amer. Chem. Soc.*, 1918, 40, 1726–1732).—A consideration of the formation of acetonedicarboxylic acid from citric

acid, of its relationships to acetone and acetoacetic acid, of the connexion between the latter and acetic acid, and of those between acetic acid and keten, leads the author to propose the electronic formulæ (I) and (II) for acetoacetic and citric acids respectively:



H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. V. Optically Active Complex Salts of Iridium-trioxalic Acid. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 21, 203—214).—Racemic potassium iridium oxalate, $\text{K}_3[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot 4\frac{1}{2}\text{H}_2\text{O}$ (A., 1918, i, 4), has been resolved into its optically active components by means of the strychnine salt, thus demonstrating for the first time the possibility of a partial asymmetry in the case of iridium as the central atom.

Strychnine d-iridium oxalate, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_2[\text{Ir}(\text{C}_2\text{O}_4)_3] \cdot 3\frac{1}{2}\text{H}_2\text{O}$, forms pale yellow, very fine needles; the corresponding *l-salt* ($+3\text{H}_2\text{O}$) crystallises in somewhat thicker needles.

d-Potassium iridium oxalate ($+ \text{H}_2\text{O}$), large orange-coloured, flattened, triangular bipyramids ($a:c=1:0.9520$; $\alpha=100^\circ 20'$), has $D^{20} 2.734$; the corresponding *l-salt* is also described. As in the case of the oppositely rotating rhodium salts (A., 1918, i, 3), a non-superposable hemihedrism accompanies the contrary power of rotation.

The specific rotation of the salts in aqueous solution for differing concentrations and for light of varying wave-length has been investigated, and the results are given in a series of tables and graphs, for details of which the original communication must be consulted. In the case of the potassium salts, the slope of the graph is quite different from that found with the corresponding rhodium salt, thus showing the preponderating influence of the special nature of the central metallic atom on the specific light absorption (colour) of these salts and on the whole character of the rotation dispersion.

H. W.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VI. The Fission of Potassium Rhodium Malonate into its Optically Active Compounds. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, 21, 215—224).—The resolution of *r-potassium rhodium malonate*, $[\text{Rh}(\text{C}_3\text{H}_2\text{O}_4)_3]\text{K}_3 \cdot 3\text{H}_2\text{O}$ (A., 1918, i, 4), is effected

through the cinchonine salts and subsequent decomposition of the latter by potassium iodide. *Cinchonine l-rhodium malonate* ($+\frac{1}{2}\text{H}_2\text{O}$) is less soluble in water and less stable to heat than the corresponding *d*-salt ($+3\text{H}_2\text{O}$). *d*- and *l*-Potassium rhodium malonates form pale yellow crystals; measurements of the *l*-salt showed the crystals to belong to the monoclinic-sphenoidal class ($a:b:c=1.0637:1.11667$, $\beta=82^\circ 27\frac{1}{2}'$), D_4^{25} 2.317.

The molecular rotation dispersion of the salts has been investigated in aqueous solution; with the potassium salts a remarkable maximum occurs at about 5800 Å.U. For wave-lengths smaller than 5800 Å.U. the rotation of the plane of polarisation increases with increasing wave-length, whilst for those greater than 5800 Å.U. it diminishes with increasing wave-lengths as in ordinary cases. In the neighbourhood of 5800 Å.U. the absorption-spectrum, however, does not manifest a single line or band. The occurrence of such anomalous rotation-dispersion seems to be theoretically explicable if the assumption may be made that at least two kinds of active ions are present.

H. W.

New Synthetic Passage from Aliphatic to Aromatic Compounds. TEL. KOMNINOS (*Compt. rend.*, 1918, 167, 781—783; *Bull. Soc. chim.*, 1918, [iv], 22, 449—455).—Malonyl chloride and acetone react together in the presence of calcium carbonate to give phloroglucinol and a compound, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COCl}$, which when boiled with water and some more calcium carbonate, in its turn is converted into phloroglucinol.

W. G.

Effect of Sodium on Mixtures of Malonic and Succinic Esters. GERALD E. K. BRANCH and H. E. HUDSON BRANCH (*J. Amer. Chem. Soc.*, 1918, 40, 1708—1713).—The investigation was undertaken in the hope of the ultimate synthesis of the compound, $\begin{array}{c} \text{CH}=\text{CH} \\ | \quad \quad | \\ \text{CH}=\text{CH} \end{array} > \text{CH}-\text{CH} < \begin{array}{c} \text{CH}=\text{CH} \\ | \quad \quad | \\ \text{CH}=\text{CH} \end{array}$, which might show a tendency to break down to give the cyclopentadienyl radicle. The condensation of ethyl malonate with ethyl succinate was studied as the first step in this direction. The results were not very promising, and the observations may be summarised as follows: (1) When molar mixtures of malonic and succinic esters are treated with sodium, the main product is succinylsuccinic ester. (2) When a large excess of malonic ester is used, phloroglucinoltricarboxylic ester is produced. (3) *Malonylsuccinic ester*, yellow crystals, m. p. 163° , is obtained from succinylsuccinic and malonic esters. The results are to be explained by an application of Dieckmann's theory of the reversibility of the acetoacetic ester condensation.

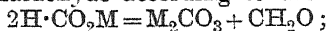
H. W.

Preparation of Derivatives of Cystine, Soluble in Water. BERNHARD STUBER (D.R.-P. 307858; from *Chem. Zentr.*, 1918, ii, 574).—The sparingly soluble compounds of cystine and its derivatives with mercury, mercury chloride, or silver are dissolved in solutions of sodium chloride, sodium bromide, sodium thio-

cyanate, or lithium chloride, and the solutions are treated with an excess of acetone, methyl or ethyl alcohol, or ether; the precipitates are filtered and dried in a vacuum. Complex salts of amphoteric character are obtained which are expected to find therapeutic application. The following substances are particularly described: *cystinemercury sodium chloride*, yellow powder; *cystinemercury sodium bromide*, brown powder; *cystinemercury lithium chloride*, yellowish-white powder; *cystinemercury sodium thiocyanate*, yellowish-brown powder; *cystinesilver sodium chloride*, brown powder; *cystinemercury chloride sodium chloride*, white powder; *cystinemercury chloride sodium bromide*, brown powder. H. W.

Reducibility of Formic Acid. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, 51, 1389—1398).—In spite of all statements in the literature to the contrary, the authors have never obtained more than 4% of the expected yield in their attempts to reduce formic acid to formaldehyde and methyl alcohol by hydrogen under the most diverse experimental conditions. The following reducing agents were tried: (i) reduction of formic acid in aqueous solution by nascent hydrogen at ordinary pressure; the hydrogen was generated by zinc in contact with mercury, cadmium, copper, and vanadium oxide, with and without the addition of dilute sulphuric acid, by zinc and palladous chloride, by zinc dust with and without the addition of palladium, and by the platinum metals; (ii) reduction of formic acid in aqueous solution by nascent hydrogen under increased pressure; the experiments under (i) were repeated in sealed tubes at 70°, the tubes being filled with carbon dioxide before sealing; (iii) reduction with simultaneous catalytic fission of the formic acid; the experiments under (ii) were repeated in the presence of platinum metals on porous tile. C. S.

Production of Formaldehyde and Methyl Alcohol from Formates. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, 51, 1398—1418. Compare preceding abstract).—In the well-known decomposition of formic acid by heat and the reaction between an alkali formate and an alkali hydroxide, the principal factor controlling the course of the reactions is the striving to produce the stable hydrogen molecule. Metallic formates, however, are able, to a degree dependent on the nature of the particular metal, to yield formaldehyde according to the equation



the secondary decomposition, $\text{CH}_2\text{O} = \text{H}_2 + \text{CO}$, can be reduced to a minimum under suitable experimental conditions, and the decomposition in the presence of water, $\text{CH}_2\text{O} + \text{H}_2\text{O} = \text{CO}_2 + 2\text{H}_2$, can be prevented altogether.

The temperature at which a distinct and sustained evolution of gas begins from the formates is in general higher the more strongly basic is the metallic oxide; thus copper formate (170°) is the first and potassium formate (375°) the last member of the series of formates examined. The formaldehyde produced experiences, according to the nature of the metalliferous residue, diverse trans-

formations, of which the most important is its conversion into methyl alcohol and formic acid. In the case of the formates of strong bases, only a little formaldehyde is obtained, the main products being methyl alcohol, acetone, furfuraldehyde, empyreumatic substances, and carbon.

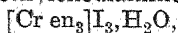
Zinc formate is the most suitable substance for the production of formaldehyde and methyl alcohol, and its decomposition is described in detail. Methyl formate has been detected in the products.

The vapour of formic acid in the presence or absence of hydrogen is converted by chemically unchangeable catalysts, such as asbestos, platinised asbestos, alumina, carbon, etc., almost exclusively into carbon monoxide and steam or carbon dioxide and hydrogen as soon as the temperature is high enough to bring the formic acid into reaction. If, however, the catalyst and the temperature of reaction are so selected that the formation of formates is rendered possible, the production of considerable quantities of formaldehyde and methyl alcohol is observed. The best catalysts for this purpose are zinc oxide and thoria. A diagram is given in which are plotted the two curves connecting the percentage of formaldehyde and the percentage of total decomposition products with the decomposition temperatures, zinc oxide being the catalyst. The two curves produced backwards meet at a point corresponding with about a 12% yield of formaldehyde and a decomposition temperature of about 245° , showing that at this temperature formaldehyde is the only primary decomposition product of formic acid. [See also *J. Soc. Chem. Ind.*, 1918, 782A.]

C. S.

The Preparation of Ethylamine and of Diethylamine. EMIL ALPHONSE WERNER (T., 1918, 113, 899—902).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VII. Optically Active Salts of the Triethylenediaminechromi-series. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Acad. Wetensch. Amsterdam*, 1918, 21, 225—230).—The molecular rotation dispersion of the optically active triethylenediaminechromi-iodides in aqueous solution at different concentrations has been investigated, and the results are given in a series of graphs and tables; the substances were obtained by Werner's method (A., 1912, i, 417). It was not found possible to obtain measurable crystals of the active salts, partly owing to their great solubility and partly because of the readiness with which they decompose in aqueous solution, particularly under the influence of light. *r*-Triethylenediaminechromi-iodide,



forms orange to red rhombic-bipyramidal crystals ($a:b:c = 0.8632:1.0:0.8652$); the crystals are pseudo-tetragonal and per-

fectly isomorphous with the corresponding crystals of the cobalt- (A., 1915, i, 867) and of the rhodium (A., 1918, i, 7) compound.

H. W.

Biochemical Properties of Aminoglucose. A. CLEMENTI (*Arch. farm. sper. Sci. off.*, 1918, 25, 225—230; from *Chem. Zentr.*, 1918, ii, 617).—Glucosamine hydrochloride behaves as a monobasic acid in the formol titration; Molisch's reaction is positive with the free base, but negative with the salts. Fermentation with brewer's yeast, without addition of toluene, is observed after more than seventy-two hours; obviously, foreign micro-organisms are active, possibly owing to deamination.

H. W.

Fluorides of Organo-metallic Compounds. I. Tin Trialkyl Fluorides and Tin Dialkyl Difluorides. ERICH KRAUSE (*Ber.*, 1918, 51, 1447—1456).—The fluorides exhibit striking differences in properties from the other tin alkyl and aryl haloids. Thus the tin trialkyl fluorides are solid, crystalline, odourless substances of high m. p., which sublime before fusing, are appreciably soluble in water, giving acid solutions, and are sparingly so in indifferent organic solvents such as benzene and ether, but dissolve more readily in the alcohols and glacial acetic acid. The tin dialkyl difluorides exhibit similar properties, and, in addition, form double compounds with alkali fluorides.

The tin trialkyl fluorides are precipitated quantitatively by treating solutions of the corresponding hydroxides (Grüttner and Krause, A., 1918, i, 158) with aqueous hydrofluoric acid, but can be obtained much more conveniently by treating alcoholic solutions of the other tin trialkyl haloids with an excess of a neutral aqueous solution of potassium fluoride. The latter reaction is reversible, and a complete reconversion of the fluoride into another tin trialkyl haloid is effected by warming with the concentrated halogen acid.

Tin dialkyl difluorides are precipitated almost quantitatively by treating alcoholic solutions of the other dihaloids with the calculated quantity of potassium fluoride in neutral aqueous solution.

The following compounds are described. All m. p.'s were determined in closed capillary tubes. *Tin trimethyl fluoride*, SnMe_3F , colourless prisms, which begin to darken at 360° and blacken at about 375° ; *tin triethyl fluoride*, prisms, m. p. 302° (corr.); *tin tri-n-propyl fluoride*, prisms or needles, m. p. 275° (corr.); *tin triisobutyl fluoride*, prisms, m. p. 244° (corr.); *tin triisamyl fluoride*, needles, m. p. 288° (corr.); *tin diethyl n-propyl fluoride*, long needles, m. p. 271° (corr.); *tin dimethyl difluoride*, colourless leaflets, decomp. above 360° ; *tin diethyl difluoride*, tufts of needles or rhombic plates, m. p. $287\text{—}290^\circ$ (uncorr.), sintering at about 240° (the double salt, $\text{SnEt}_2\text{F}_2 \cdot 2\text{KF}$, forms stout leaflets); *tin di-n-propyl difluoride*, leaflets, m. p. $204\text{—}205^\circ$ (uncorr.), sintering at 200° .

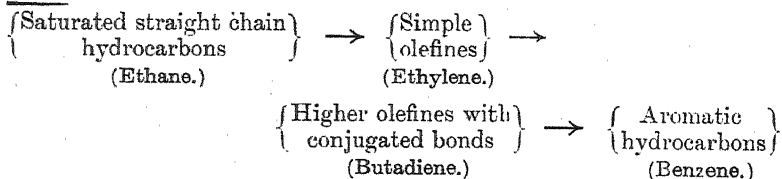
The tin trialkyl fluorides, which are easily obtained pure, are

b *

available for the preparation of mixed tin tetra-alkyls, tin triethyl *n*-propyl, for example, being obtained from magnesium *n*-propyl chloride and tin triethyl fluoride in the usual way; the odour of the volatile tin trialkyl chloride is always observed, indicating that a partial exchange of the halogen atoms occurs.

Tin tetraisoamyl, prepared from tin tetrachloride and magnesium isoamyl chloride, and freed from any tin trialkyl haloid by aqueous-alcoholic potassium fluoride, has b. p. $188^{\circ}/24$ mm., $D_4^{19.6}$ 1.0353, n_D 1.46946, n_D 1.47242, n_D 1.47989, n_D 1.48607 at 16.0° . C. S.

Formation of Aromatic Hydrocarbons from Natural Gas Condensates. J. G. DAVIDSON (*J. Ind. Eng. Chem.*, 1918, **10**, 901—910).—Natural gas containing chiefly ethane and propane with small quantities of butane and pentane has been subjected to the "cracking" process at various temperatures in the presence of metals. The products of the reaction are gaseous and liquid, the latter being of a tarry nature and containing aromatic hydrocarbons. Both sets of products were analysed, and the results are tabulated in the paper. The experiments show that most metals are without action on the reaction. Paraffins \rightarrow aromatic hydrocarbons. The metals nickel, iron, and cobalt are negative catalysts for the above reaction, but accelerate markedly the reaction paraffins \rightarrow carbon + hydrogen. The effect of pressure and temperature on the reaction has been studied, and it is shown that the temperature 850° is the most favourable for the production of liquid tar, and that the formation of complex aromatic substances increases with the temperature. Increase of pressure inhibits the formation of tar, whilst diminished pressure increases the yield of unsaturated substances, but also decreases the actual yield of tar. Butadiene has been isolated in fairly large amounts from the unsaturated compounds produced in the thermal decomposition of the natural gas condensate. Acetylene is without action in the formation of aromatic hydrocarbons. Tar containing aromatic substances has been produced from the "cracking" of a mixture of butadiene and ethylene. The most probable reaction for the formation of aromatic substances from natural gas condensate is:



J. F. S.

Dinitro-derivatives of *p*-Dichlorobenzene. 1:4-Dichloro-2:5-dinitrobenzene. EDITH H. NASON (*J. Amer. Chem. Soc.*, 1918, **40**, 1602—1605).—Of the possible 1:4-dichlorodinitrobenzenes, 1:4-dichloro-2:6-dinitrobenzene, m. p. 104° , has been

previously described and fully orientated; a second isomeride, m. p. 101° , has also been obtained, but its constitution has not been elucidated. The author now shows that all three isomerides are formed when *p*-dichlorobenzene is nitrated with a mixture of concentrated sulphuric and fuming nitric acids, and that the chief product is the previously unknown 1:4-dichloro-2:5-dinitrobenzene, fine, yellow needles, m. p. 81° . The constitution of the compound is deduced from its reduction to 2:5-dichloro-*p*-phenylenediamine (compare Mohlau, A., 1886, 941), and confirmed by oxidation of the latter substance to *p*-dichlorobenzoquinone, yellow crystals, m. p. 161° .

The isomeride, m. p. 101° , must therefore be 1:4-dichloro-2:3-dinitrobenzene. H. W.

***s*-Chlorobenzenedisulphonic Acid and some of its Derivatives.** S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 307—314).—When chlorobenzene is heated with five times its volume of fuming sulphuric acid, containing 20% of sulphur trioxide, at 300° for six hours, the product is 5-chlorobenzene-1:3-disulphonic acid, decomposing at 100° , isolated as its barium salt, $C_6H_5Cl(SO_3)_2Ba, 3H_2O$. It gives a potassium and an ammonium salt, a dichloride, m. p. 105.5 — 106° , and a diamide, m. p. 223 — 224° . The dichloride, when heated in a sealed tube with phosphorus pentachloride for four hours at 200 — 210° , yields *s*-trichlorobenzene.

4-Aminobenzene-1:3-disulphonic acid, when diazotised in hydrochloric acid solution and the diazonium salt decomposed with finely divided copper, gives 4-chlorobenzene-1:3-disulphonic acid isolated as its potassium salt. It gives a dichloride, an amorphous compound, and a diamide, m. p. 217 — 219° . W. G.

Studies in the Tetrahydronaphthalene Series. ARTHUR G. GREEN and FREDERICK MAURICE ROWE (*T.*, 1918, **113**, 955—973).

Mono- and Di-chlorophenanthrenes. HÅKAN SANDQVIST and A. HAGELIN (*Ber.*, 1918, **51**, 1515—1526).—A solution of phenanthrene (containing anthracene; m. p. 97 — 102°) in carbon disulphide or carbon tetrachloride at 0° is treated slowly with an unsaturated solution of chlorine (about $1\frac{1}{2}$ mols.) in the same solvent at 0° . In addition to unchanged phenanthrene the substances obtained are (1) a compound (? trichloroanthracene), pale yellow needles, m. p. 365° (corr.), (2) 9:10-dichloroanthracene (previously described by Sandqvist in 1917 as a dichlorophenanthrene, m. p. 208 — 209°), (3) phenanthrene 9:10-dichloride, (4) 10-chlorophenanthrene, (5) pitch.

Phenanthrene 9:10-dichloride, $C_{14}H_{10}Cl_2$, decomposes appreciably into 10-chlorophenanthrene and hydrogen chloride at the ordinary temperature in the course of a few days, the decomposition being catalytically accelerated by 10-chlorophenanthrene. The m. p. is

therefore variable; a carefully purified specimen had m. p. 161° (corr.; bath at above 150° and rapidly heated), and hydrogen chloride was liberated.

Pure 10-chlorophenanthrene can be prepared from the preceding dichloride at 150 – 175° . It forms long, colourless needles, m. p. 53 – 53.5° (corr.), b. p. 370° (corr.)/737 mm., D_4^{25} 1.2310 and D_4^{20} 1.2163. It yields phenanthraquinone by oxidation, and forms a *picrate*, $C_{14}H_9Cl \cdot C_6H_3(NO_2)_3 \cdot OH$, yellow, prismatic needles, m. p. 115° (corr.).

9:10-Dichlorophenanthrene, m. p. 160 – 160.5° , which is formed by chlorinating 10-chlorophenanthrene in cold carbon disulphide or tetrachloride, yields phenanthraquinone by oxidation with boiling acetic and chromic acids.

The 3:10-dichlorophenanthrene, m. p. 124° , obtained by Sandqvist (A., 1909, i, 779) is now proved to be I-3(or 6):10-dichlorophenanthrene, m. p. 125 – 125.5° (corr.), by its formation by heating I-10-chlorophenanthrene-3(or 6)-sulphonyl chloride with phosphorus pentachloride; it yields 3-chlorophenanthraquinone, orange-yellow needles, m. p. 261° (corr.) (*monoxime*, $C_{14}H_9O_2NCl$, yellow needles, m. p. 204° [decomp.]), by oxidation with chromic and acetic acids.

An aqueous solution of potassium phenanthrene-3-sulphonate on treatment at 50° with a cold saturated aqueous solution of chlorine yields *potassium II-10-chlorophenanthrene-3(or 6)-sulphonate*, small needles, which is converted by phosphorus pentachloride into *II-10-chlorophenanthrene-3(or 6)-sulphonyl chloride*, grey, crystalline powder, m. p. 171° , from which *II-10-chlorophenanthrene-3(or 6)-sulphonic acid*, m. p. 207° , is obtained by the action of water at 140 – 150° , and *II-3(or 6):10-dichlorophenanthrene*, colourless needles, m. p. 113° , by the action of phosphorus pentachloride. The last-mentioned compound yields 3-chlorophenanthraquinone by oxidation. (The prefixes I and II indicate: I, that the compound contains substituents having the same orientation as those in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the sulphonation of 10-bromophenanthrene; II, that the orientation of the substituents in the compound is the same as in the 10-bromophenanthrene-3(or 6)-sulphonic acid obtained by the bromination of phenanthrene-3-sulphonic acid).

C. S.

Acetylation of *p*-Iodoaniline by Acetic Anhydride. P. J. MONTAGNE (*Ber.*, 1918, 51, 1489–1492).—*p*-Iodoaniline, which is very conveniently prepared by treating a solution of *p*-iodonitrobenzene in acetone with a solution of stannous chloride in hydrochloric acid (D 1.19) and basifying after the acetone has spontaneously boiled, is converted by acetic anhydride into *p*-iodoacetanilide if the mixture is gently warmed, but into *p*-iodoacetanilide and *p*-iododiacetanilide if the mixture is boiled for one-quarter to six hours; a small quantity of a *substance*, leaflets, m. p. 204.5° , is also obtained.

p-Iodoacetanilide has m. p. about 170° (rapidly heated) and 184.5° (slowly heated).

C. S.

Analgesic Substance and Process of Making. LAMBERT THORP (U.S. Pat., 1279942).—Anilides of α -bromo- α -ethylbutyric acid are prepared by treating arylamines with an acylhaloid of the acid. These anilides possess analgesic and sedative properties; they are decomposed on boiling with alkali hydroxide, the bromine being eliminated as alkali bromide. In particular, the *p*-phenetidine of α -bromo- α -ethylbutyric acid is specified; this is a colourless, crystalline compound slightly soluble in water, readily so in alcohol or ether, m. p. 54° . It has a peculiar, somewhat bitter taste. (See also *J. Soc. Chem. Ind.*, 1918.) J. F. B.

Trimorphic Change of 4-Nitroaceto-*o*-toluidide. FREDERICK DANIEL CHÁTTAWAY (T., 1918, 113, 897—899).

The *n*-Butylarylamines. I. The Action of *n*-Butyl Chloride on *o*- and *p*-Toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, 113, 974—985).

The *n*-Butylarylamines. II. Nitration of Mono- and Di-*n*-butyl-*p*-toluidines. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, 113, 985—995).

Nitro-derivatives of Diphenylamine. HUGH RYAN and THOMAS GLOVER (*Proc. Roy. Irish Acad.*, 1918, 34, [B], 97—105).—Considerable discrepancies are frequently noticed in the literature of the nitrodiphenylamines. With the object of removing these, the authors have prepared a series of substances by synthetic methods, that due to Goldberg (A., 1907, i, 1027) (in which aromatic amines are coupled with the halogen derivatives of aromatic nitro-compounds in nitrobenzene solution in the presence of potassium carbonate and cuprous iodide) being chiefly used. The following compounds are described: *p*-Nitrodiphenylamine, m. p. 133 — 134° , which, contrary to Goldberg's statement, yields a colourless solution in concentrated sulphuric acid; *m*-nitrodiphenylnitrosoamine, colourless, acicular crystals, m. p. 89 — 90° ; 2:4-dinitrodiphenylnitrosoamine, pale yellow prisms, m. p. 149 — 151° (by the action of isoamyl nitrite on a cold solution of 2:4-dinitrodiphenylamine in glacial acetic acid; at a slightly higher temperature, 2:4:2':4'-tetranitrodiphenylamine slowly separates); 3:4'-dinitrodiphenylamine, pale yellow crystals, m. p. 210 — 212° , after softening at 205° ; 2:4:6-trinitrodiphenylamine, scarlet-red prisms, m. p. 178° ; 2:4:3'-trinitrodiphenylamine, brown, platy crystals, m. p. 193 — 194° ; nitrophenyl-2:4-dinitro-*m*-tolylamine, dark yellow prisms, m. p. 199° (slight decomp.); 4-nitrophenyl-2:4-dinitro-*m*-tolylamine, straw-coloured, prismatic needles, m. p. 210° (slight decomp.); 3-nitrophenyl-2:6-dinitro-*m*-tolylamine (?), prismatic needles, m. p. 199° (decomp.); 2:4:2':4'-tetranitrodiphenylamine, brown prisms, m. p. 199 — 200° ; 2:4:6:3'-tetranitrodiphenylamine, short, yellow prisms, m. p. 210° (corr.); 2:4:6:4'-tetranitrodiphenylamine, golden-yellow prisms, m. p. 222° .

m-Nitrodiphenylnitrosoamine is converted by nitric acid in glacial acetic acid solution into trinitrodiphenylnitrosoamine, yellow, pris-

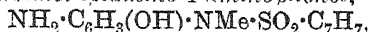
matic needles, m. p. 184—185° (decomp.), after softening at about 179°.

2:4:3'-Trinitrodiphenylamine yields *tetranitrodiphenylamine*, yellow crystals, m. p. 190°, when treated with *isoamyl* nitrite. In similar circumstances, picryl-aniline gives two compounds, one of which, m. p. 236°, is probably 2:4:6:2':4':6'-*hexanitrodiphenylamine*, whilst the other, m. p. 193—194°, appears to be 2:4:6:2':4'-*pentanitrodiphenylamine*. H. W.

The Freezing Points of Mixtures of Phenol, *o*-Cresol, *m*-Cresol, and *p*-Cresol. HARRY MEDFORTH DAWSON and CHRISTOPHER ARCHIBALD MOUNTFORD (T., 1918, 113, 923—935).

Preparation of Hydroxy-alkyl Ethers of *p*-Acetylaminophenol or Substitution Products thereof. JOSEPH TCHERNIAC (Brit. Pat., 120081).—An alkylene or hydroxy-alkylene monohalogen-hydrin, for instance, ethylene or glycerol monochlorohydrin, is heated in water with *p*-acetylaminophenol or a substitution derivative thereof, in the presence of an equivalent quantity of alkali to combine with the halogen hydracid. For instance, 151 parts of *p*-acetylaminophenol are dissolved in an exactly equivalent quantity of 2*N*-sodium hydroxide solution, while cooling and shaking, and 81 parts of ethylene chlorohydrin are added; the mixture is heated at 60—70° for eight hours, and the β -hydroxyethyl ether separates as an oil, which crystallises on cooling. The yield is 85—90% of the theoretical, and the substance is purified by crystallising from hot water with treatment with animal charcoal. [See also *J. Soc. Chem. Ind.*, 1919, Jan.] J. F. B.

Transformation of Arylhydroxylamines into Amino-phenols. F. KLAUS and O. BAUDISCH (*Ber.*, 1918, 51, 1228—1230).—Finely powdered 3-*p*-toluenesulphonylmethylaminophenylhydroxylamine is added to a mixture of concentrated sulphuric acid and ice, water is added, and the whole is heated first on the water-bath and finally over a naked flame; the solution is filtered, neutralised with sodium carbonate, and sodium acetate is added, whereby 2-*p*-toluenesulphonylmethylamino-4-aminophenol,



m. p. 163—164°, is obtained. It develops a violet coloration with ferric chloride, reduces ammoniacal silver oxide solution, and after diazotisation couples with phenols.

In a similar manner *o*-hydroxylaminophenyl *p*-toluenesulphonate is converted into 2-amino-5-hydroxyphenyl *p*-toluenesulphonate, which is obtained in the form of the *sulphate*, colourless crystals, m. p. 162°; the *hydrochloride* forms colourless needles, m. p. 187—190°.

C. S.

A Compound of Strontium Bromide and Sodium Benzoate in Galenical Pharmacy. E. CANALS and J. SERRE (*Schweiz. Apoth. Zeit.*, 56, 318—319; from *Chem. Zentr.*, 1918, ii, 468).

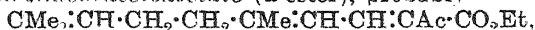
—*Strontium benzoate*, $(\text{PhCO}_2)_2\text{Sr}\cdot 3\text{H}_2\text{O}$, is obtained in small, transparent, hygroscopic needles, m. p. 410° , by mixing solutions of sodium bromide (20 grams), strontium bromide (20 grams), and sodium benzoate (12 grams), each dissolved in water (50 c.c.), diluting the mixture with an additional 150 c.c. of water, and allowing it to remain for twenty-four hours; the product is repeatedly crystallised from small quantities of hot water. At 15° , 1 part of the salt dissolves in 25.9 parts of water. H. W.

Basic Zirconyl Benzoates and Salicylates. F. P. VENABLE and F. R. BLAYLOCK (*J. Amer. Chem. Soc.*, 1918, **40**, 1746—1748). —The salts were prepared by precipitating a hot aqueous solution of zirconyl chloride with a similar solution of benzoic acid and subsequent washing with hot water. Analyses of different samples of the benzoate appear to show that under varying conditions as to concentration, etc., no single definite compound is formed. The precipitates have varying ratios between the acid radicle and the partly dehydrated zirconium hydroxide. The salicylates are notably less stable; they turn brown at 100° and become black at 160° . They appear to exhibit a tendency to form only one basic compound, in spite of varying conditions of formation, showing therein a difference from the precipitates formed with benzoic acid. H. W.

Preparation of 4-Sulphoaminobenzene-2-carboxylic [6-Amino-*m*-sulphobenzoic] Acid. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 307284, additional to D.R.-P. 296941; from *Chem. Zentr.*, 1918, ii, 574).—6-Amino-*m*-sulphobenzoic acid is conveniently prepared by the action of molecular amounts of chlorosulphonic acid and anthranilic acid dissolved in sulphuric acid monohydrate. The mixture is slowly heated to 90 – 100° , and subsequently to 130 – 140° after evolution of hydrogen chloride has ceased. Under these conditions, the monohydrate has practically no sulphonating action. H. W.

--Citral Series. Condensation of Citral with Acetoacetic Ester. E. KNOEVENAGEL [with PAUL SEHLER, WILHELM STÖTZNER, RUDOLF STEINLE, GUSTAV MECHTERSHEIMER, WILHELM MAMONTOFF, and ADOLF STANG] (*J. pr. Chem.*, 1918, [iii], **97**, 288—335).—Five isomeric ethyl citrylideneacetoacetates have been obtained, the constitution of none of which has yet been definitely determined.

Ethyl citrylideneacetoacetate (α -ester), probably

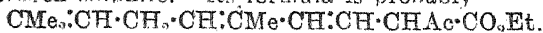


a pale yellow, faintly odorous liquid, b. p. $186^\circ/12$ mm., D_4^{20} 1.0202, n_D^{20} 1.4835, n_D^{25} 1.50645, is obtained by adding 72 drops of piperidine to a mixture of equal molecular quantities of ethyl acetoacetate and citral at about -15° , and keeping in the cold for about forty-eight hours. It changes partly to the β -ester (below) by repeated distillation or by prolonged exposure to light, dissolves easily in aqueous sodium hydrogen sulphite (therefore a double linking is

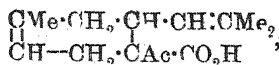
adjacent to a carbonyl group), and forms an oily *hydrobromide*, which is converted by boiling sodium carbonate solution into *ethyl α-isocitrylideneacetoacetate* (*terpinolenylacetoacetate*). This ester, which probably has the constitution $\text{CMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CHX} \\ \text{CH} - \text{CH}_2 \end{smallmatrix} > \text{C} : \text{CMe}_2$

or $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CHX} \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix} > \text{C} : \text{CMe}_2$ (where $\text{X} = \text{CHAc} \cdot \text{CO}_2\text{Et}$), forms colourless, rhombic plates, m. p. 69° , b. p. $164^\circ/12 \text{ mm.}$, $D_4^{20} 1.0056$, and is also obtained by heating the α -ester with a few c.c. of 30% sulphuric acid on the water-bath. By the addition of hydrogen bromide to the α -isoester and its removal again by sodium carbonate, the α -isoester is regenerated. The α -isoester is difficultly hydrolysed, but is converted into α -isocitrylideneacetoacetic (*terpinolenylacetoacetic*) acid, crystals, m. p. 175° (with evolution of carbon dioxide), by alcoholic potassium hydroxide at 150° , or by very concentrated, boiling aqueous potassium hydroxide. The acid, the silver salt of which reacts with ethyl iodide to form the α -isoester, is converted by heating at 180° into α -isoionone (*terpinolenylacetone*), $\text{C}_{13}\text{H}_{20}\text{O}$, a faintly yellow oil, b. p. $122^\circ/23 \text{ mm.}$, $D_4^{20} 0.9500$, $n_D^{20} 1.5021$ (*semicarbazone*, colourless crystals, m. p. 205° [decomp.]), and is converted by 10% potassium permanganate and a slight excess of sodium carbonate below 3° into a saturated acid, $\text{C}_{14}\text{H}_{24}\text{O}_5$, crystals, m. p. 192° , but yields, when a little more permanganate is used, an acid, $\text{C}_{12}\text{H}_{22}\text{O}_4$, needles, m. p. 183.5° . The latter acid is converted by boiling water into a substance, $\text{C}_{12}\text{H}_{20}\text{O}_3$, m. p. 111° (*p-bromophenylhydrazone*, m. p. 174°), and by heating in a vacuum into an isomeric substance, m. p. 94° , b. p. $180^\circ/23 \text{ mm.}$, which changes into the substance, m. p. 111° , by keeping. The oxidation of the α -isoester by chromic and acetic acids below 3° yields a substance, $\text{C}_{13}\text{H}_{18}\text{O}_4$, m. p. 42° , which forms a *semicarbazone*, yellowish-white needles, m. p. 193° . α -Isoionone is oxidised by the preceding reagent to a substance, $\text{C}_{12}\text{H}_{18}\text{O}_3$, b. p. $168-171^\circ/22.5 \text{ mm.}$, m. p. 58° .

Ethyl citrylideneacetoacetate (β -ester), obtained by the repeated distillation of the α -ester in a vacuum and heating the product for eight hours at about 180° in a vacuum, or at about $230^\circ/\text{atm.}$, has b. p. $168^\circ/12 \text{ mm.}$, $D_4^{20} 1.0329$, $n_D^{20} 1.5072$, and is insoluble in alkali hydrogen sulphite. Its formula is probably

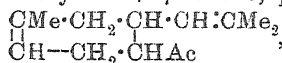


It is hydrolysed by boiling concentrated aqueous potassium hydroxide, yielding β - ψ -citrylideneacetoacetic acid, probably



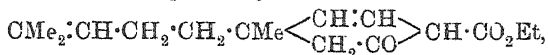
crystals, m. p. 138° (decomp.), which by esterification by alcohol and 25% sulphuric acid at about 60° yields *ethyl β-ψ-citrylideneacetoacetate*, $\text{C}_{16}\text{H}_{24}\text{O}_3$, crystals, m. p. $99-100^\circ$, from which the β - ψ -acid is regenerated by hydrolysis. By oxidation with alkaline 1% permanganate (6 atoms of oxygen) below 5° , the β - ψ -acid yields an unsaturated acid, $\text{C}_8\text{H}_{12}\text{O}_3$, probably γ -methyl- Δ^2 -butenylpyruvic

[ϵ -methyl- Δ^8 -hepten- α -onic] acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, needles, m. p. 192° (decomp.), which reduces warm ammoniacal silver oxide solution. By heating above its m. p., the β - ψ -acid loses carbon dioxide and yields β - ψ -ionone, probably

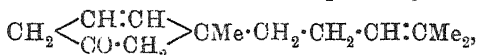


b. p. $125^\circ/19$ mm., D_4^{17} 0.9594, D_4^{22} 0.9547, n_D^{17} 1.49785 (semicarbazone, m. p. 152°).

The β -ester forms a hydrobromide, $\text{C}_{16}\text{H}_{25}\text{O}_3\text{Br}$, crystals, m. p. $93-94^\circ$, and is converted by heating with zinc chloride at 180° into β -ionene, $\text{C}_{13}\text{H}_{18}$, an oil with a characteristic odour, b. p. $63^\circ/12$ mm., D_4^{20} 0.8619, n_D^{20} 1.4904. The preceding hydrobromide is converted by boiling aqueous sodium carbonate into ethyl β -isocitrylideneacetoacetate, probably

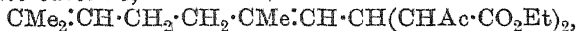


b. p. $160-161^\circ/12$ mm., D_4^{20} 1.0397, n_D^{20} 1.5082, which is insoluble in alkali hydrogen sulphite, regenerates the preceding hydrobromide, and by hydrolysis with boiling concentrated potassium hydroxide solution yields β -isocitrylideneacetoacetic acid, $\text{C}_{14}\text{H}_{20}\text{O}_3$, colourless crystals, m. p. 153° . This acid, the silver salt of which reacts with ethyl iodide to form the β -isoester, is converted by heating at about 160° into β -isoionone, probably



b. p. $113^\circ/15$ mm., D_4^{20} 0.9481, n_D^{20} 1.4929, which forms a semicarbazone, crystals, m. p. 108° , and p-bromophenylhydrazone, crystals, m. p. $150-152^\circ$.

The reaction between citral and ethyl acetoacetate (2 mols.) below 0° in the presence of a little piperidine yields ethyl citrylidenebisacetoacetate,

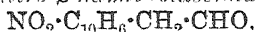


colourless crystals, m. p. 64° , which forms an oxime, $\text{C}_{22}\text{H}_{35}\text{O}_6\text{N}$, crystals, m. p. 164° , and is converted by boiling alcoholic potassium hydroxide into 1-methyl-5- β -dimethyl- $\Delta^{\alpha\alpha}$ -heptadienyl- Δ^1 -cyclohepten-3-one, $\text{C}_9\text{H}_{15}\cdot\text{CH}\begin{array}{c} \text{CH}_2-\text{CO} \\ \text{CH}_2\cdot\text{CMe} \end{array}\text{CH}$, b. p. $197-198^\circ/15$ mm., D_4^{20} 0.933, D_4^{15} 0.932, n_D^{20} 1.50846. The last compound is reduced by sodium and warm alcohol to the corresponding cyclohexanol, $\text{C}_{16}\text{H}_{28}\text{O}$, b. p. $163-164^\circ/11$ mm., D_4^{15} 0.900, n_D^{15} 1.49182, which is oxidised by chromic acid to the corresponding cyclohexanone, $\text{C}_{16}\text{H}_{26}\text{O}$, b. p. $172^\circ/15$ mm., D_4^{15} 0.907, n_D^{15} 1.49163, and is converted by phosphoric oxide at 190° into the cyclohexene, $\text{C}_{16}\text{H}_{26}$, b. p. $143-144^\circ/15$ mm., D_4^{15} 0.923, n_D^{15} 1.4988. C. S.

Naphthylacetic Acids. III. 1-Nitro- β -naphthylpyruvic Acid and 1-Nitro- β -naphthylacetic Acid. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1918, 51, 1239-1245. Compare A., 1918, i, 339).—1-Nitro- β -naphthylpyruvic acid is oxidised by

alkaline potassium permanganate to 1-nitro- β -naphthaldehyde, leaflets, m. p. 99° (small yield), and a *nitronaphthoic acid*, m. p. 239° , which is not identical with any of those described by Ekkestrand in 1885. The acid, which is also obtained by oxidising 1-nitro- β -naphthylpyruvic acid by bromine in alkaline solution, yields Friedländer and Littner's 1-amino- β -naphthoic acid, m. p. $202\text{--}205^\circ$, by reduction with ferrous sulphate and hot aqueous ammonia.

1-Nitro- β -naphthylpyruvic acid is reduced to α -naphthindole-2-carboxylic acid, m. p. 213° (Schlieper gives 202°), by ferrous sulphate and aqueous ammonia or by sodium amalgam, and is converted by hot dilute hydrochloric acid and sodium nitrite (1 mol.) into a substance, m. p. 131° , which appears to be 1-nitro- β -naphthylacetoneitrile, $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}_2\cdot\text{CN}$. By treatment with dilute aqueous sodium hydroxide and subsequent distillation with steam, 1-nitro- β -naphthylpyruvic acid yields, in addition to a little nitromethylnaphthalene, a substance the bisulphite compound of which gives α -naphthisatin when decomposed by boiling dilute sulphuric acid, and 1-nitro- β -naphthylacetaldehyde,

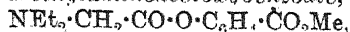


m. p. 212° , by treatment with dilute sulphuric acid in the cold. The last substance reacts with phenylhydrazine to form a *phenylhydrazone*, m. p. 162° , which appears to have the formula $\text{NO}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, since it contains an additional atom of oxygen.

1-Nitro- β -naphthylacetic acid is reduced to α -naphthoxindole by ferrous sulphate and aqueous ammonia. C. S.

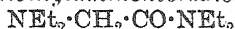
Synthesis of Derivatives of Diethylaminoacetylsalicylic [*o*-Diethylaminoacetoxybenzoic] Acid. FRIEDRICH L. HAHN and MILLY LOOS (*Ber.*, 1918, 51, 1436—1447).—The following compounds have been prepared partly to obtain substances possessing certain advantages over aspirin and partly to ascertain how the presence of substituents in the acetoxy-group affects the stability of this group. With regard to the second point, the stability appears to be increased by substituents which weaken the acidity of the acetyl group.

Methyl o-chloroacetoxybenzoate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, m. p. 62° , b. p. $195\text{--}200^\circ/30$ mm., prepared from methyl salicylate, chloroacetyl chloride, and dimethylaniline in the cold, is converted by sodium iodide in acetone solution into the corresponding *iodo*-compound, which in cold ethereal solution reacts with diethylamine to form, after treatment of the product in ethyl acetate solution with hydrogen chloride (not an excess), the *hydrochloride*, m. p. 131° , of *methyl o-diethylaminoacetoxybenzoate*,



crystals, m. p. $58\text{--}59^\circ$ (*picrate*, crystals, m. p. 147°). The *ethyl ester*, $\text{C}_{15}\text{H}_{17}\text{O}_4\text{N}$, b. p. $136\text{--}146^\circ/11$ mm., prepared from *ethyl o-chloroacetoxybenzoate*, m. p. 67° , b. p. $130^\circ/25$ mm., forms a *picrate*, needles, m. p. 138° , and *platinichloride*, m. p. $161\text{--}162^\circ$.

Diethylamine reacts with methyl *o*-chloroacetoxybenzoate to form methyl salicylate and *diethylaminoacetodiethylamide*,



(*picrate*, crystals, m. p. 133°), and with chloroacetyl chloride in ether at 0° to form *chloroacetodiethylamide*, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{NEt}_2$, b. p. $190\text{--}195^\circ/25$ mm. The last compound is converted into the corresponding *iodo*-compound, which reacts with ethereal diethylamine to form *diethylaminoacetodiethylamide*.

o-Chloroacetoxybenzoyl chloride, m. p. 55° , b. p. $165\text{--}170^\circ/12$ mm., prepared from the acid and phosphorus pentachloride and phosphorvl chloride, is converted into the *anilide*, m. p. 121° , and the latter into *o*-iodoacetoxybenzanilide, colourless crystals, m. p. 128° , which reacts with diethylamine in ethyl acetate solution to form *o*-diethylaminoacetoxybenzanilide, m. p. $129\text{--}130^\circ$ (*hydrochloride*, m. p. $131\text{--}133^\circ$).

o-Chloroacetoxybenzamide, colourless needles, m. p. 160° , is obtained from *o*-chloroacetoxybenzoyl chloride and ammonium carbonate or ethereal ammonia, or from salicylamide and chloroacetyl chloride in the presence of dimethylaniline. *o*-chloroacetoxybenzochloroacetamide, $\text{CH}_2\text{Cl} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, colourless needles, m. p. $133\text{--}134^\circ$, being an intermediate product in the last method of preparation. *o*-Iodoacetoxybenzamide has decomp. $138\text{--}139^\circ$.

o-Diethylaminoacetoxybenzamide, crystals containing $\frac{1}{2}\text{H}_2\text{O}$, m. p. $144\text{--}145^\circ$, forms a *hydrochloride*, m. p. $195\text{--}196^\circ$, which reacts with sodium nitrite in cold concentrated aqueous solution to form a substance, m. p. about 110° , which is apparently the impure *nitrite*.

C. S.

Reduction of Methyl Formylphenylacetate to Methyl Tropate. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, 51, 1237—1238).—An ethereal solution of methyl formylphenylacetate is reduced by aluminium amalgam and water (compare Müller, A., 1918, i. 223), whereby *methyl tropate*, $\text{C}_{10}\text{H}_{12}\text{O}_3$, colourless needles, m. p. $36\cdot5\text{--}37\cdot5^\circ$, b. p. $159\text{--}162^\circ/19$ mm., is obtained, which yields tropic acid, m. p. $117\text{--}118^\circ$, by hydrolysis.

C. S.

Action of Phosphorus Pentachloride on Formylphenylacetic Ester. WILHELM WISLICENUS and ERNST A. BILHUBER (*Ber.*, 1918, 51, 1366—1371).—Börner (*Diss.*, Würzburg, 1899) and Koltscharsch (*Diss.*, Würzburg, 1901) have shown that ethyl formylphenylacetate (liquid α -ester) behaves as a true aldehyde, not as a hydroxymethylene compound, towards phosphorus pentachloride, yielding impure ethyl $\beta\beta$ -dichloro- α -phenylpropionate. A purer product is obtained from the α -methyl ester. *Methyl $\beta\beta$ -dichloro- α -phenylpropionate*, $\text{CHCl}_2 \cdot \text{CHPh} \cdot \text{CO} \cdot \text{Me}$, has b. p. $137\text{--}141^\circ/23$ mm., yields β -chloro- α -phenylacrylic (chlorotropic) acid by boiling with water, and is converted by alcoholic sodium methoxide into *methyl $\beta\beta$ -dimethoxy- α -phenylpropionate*, $\text{C}_9\text{H}_{11}\text{O}_4$, m. p. $46\text{--}47^\circ$, b. p. $135\text{--}142^\circ/13$ mm.

C. S.

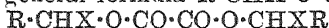
Studies in the Phenylsuccinic Acid Series. VII. The Action of Alcohols and Amines on *r*-Diphenylsuccinic Anhydride. HENRY WREN and HOWELL WILLIAMS (*T.*, 1918, 113, 832—840).

Preparation of a Calcium Tannate Sparingly Soluble in Dilute Acids. KNOLL & Co. (D.R.-P. 306979 and 307857; from *Chem. Zentr.*, 1918, ii, 494, 694).—If basic calcium tannate is heated for some time at a high temperature, it becomes sparingly soluble in dilute acids; a preparation which had been heated for six hours at 140—150° had the composition $\text{Ca}(\text{OH})\text{C}_{14}\text{H}_9\text{O}_4$, and is recommended for treatment of dysentery.

The modification described in the second patent consists in heating solutions of tannic acid with the quantity of calcium hydroxide necessary for the production of the desired basic salt until the requisite sparing solubility of the basic calcium tannate in dilute acids is attained.

H. W.

The Reaction between Acid Haloids and Aldehydes. ROGER ADAMS and E. H. VOLLWEILER (*J. Amer. Chem. Soc.*, 1918, 40, 1732—1746).—The action of benzoyl bromide, of benzoyl chloride and a number of its substitution products, and of oxalyl bromide on aromatic aldehydes has been studied. The general method was to allow the mixtures to remain at the ordinary temperature until solidification occurred, a solvent, however, being occasionally used, more particularly in conjunction with oxalyl bromide. The substances obtained proved to be halogen-substituted esters of the general formula $\text{R}\cdot\text{CHX}\cdot\text{O}\cdot\text{COR}$, or



if oxalyl haloids had been used. They are all decomposed by water into aldehyde, organic acid, and halogen acid, but the difference in the rate of decomposition is very marked; thus, the compound from benzoyl bromide and anisaldehyde decomposes within a few seconds in moist air, whilst the nitrobenzoyl chlorides form compounds which are stable for a long time in cold water. The further reactions and the constitution of these compounds have been studied mainly at the instance of α -bromobenzyl benzoate (from benzoyl bromide and benzaldehyde). This compound is slowly decomposed by cold alcohol, yielding benzaldehyde, hydrogen bromide, and ethyl benzoate, and by an ethereal solution of ammonia, giving benzamide, benzaldehyde, and ammonium bromide; with aniline in dry ethereal solution, it yields α -bromobenzylaniline and benzoic acid. Its constitution follows from its conversion into benzylidene dibenzoate by the action of silver benzoate.

Benzoyl bromide has been condensed with the following aldehydes, the m. p.'s of the products being placed within brackets: α -bromobenzaldehyde (106—107°); m -bromobenzaldehyde (110°); nitroanisaldehyde (101—102°); acetylvainillin (102—103°); p -nitrobenzaldehyde (89—90°); bromopiperonal (108—113°); with

vanillin or salicylaldehyde, a vigorous action occurred, but the hydroxy-group was attacked; anisaldehyde (oily); with terephthalaldehyde, a pure product was not obtained; with piperonal, methylsalicylaldehyde, and methylvanillin the products were too unstable to permit purification.

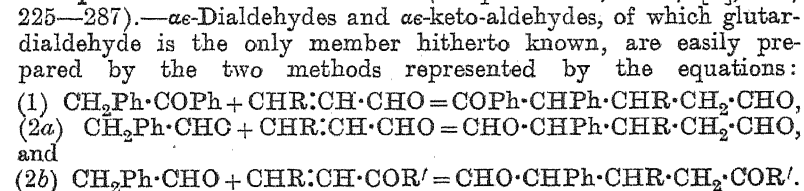
Bromovanillin methyl ether and bromopiperonal react with benzoyl chloride, yielding *substances*, m. p.'s 158—160° and 97—102° respectively, whilst the crystals from benzaldehyde and *o*-, *m*-, and *p*-nitrobenzoyl chlorides have the respective m. p.'s 81—82°, 87—88°, 118—118·5°. Solid substances could not be obtained from benzaldehyde and *p*-chlorobenzoyl chloride, *p*-bromobenzoyl bromide, or *o*-bromobenzoyl chloride.

Oxalyl bromide has been allowed to react with the following aldehydes: benzaldehyde (130—131°); *o*-bromobenzaldehyde (140°); cinnamaldehyde (85—86°); anisaldehyde (ca 66° [decomp.]); nitroanisaldehyde (116—118°); *m*-nitrobenzaldehyde (128—129°); piperonal (81—83°); vanillin (93—95°); acetylvanillin (142—143°); furfuraldehyde (76—77°). Reaction was not observed with *p*-nitrobenzaldehyde.

α -Bromobenzyl benzoate yielded benzylidene dibenzoate, m. p. 62—63°, with silver benzoate, and *benzylidene acetate benzoate*, m. p. 71—72°, with silver acetate; similarly, *benzylidene benzoate p-nitrobenzoate*, m. p. 65—67°, was prepared from α -chloro-*p*-nitrobenzyl benzoate and silver benzoate.

α -Bromobenzyl benzoate reacted with *o*-toluidine in the same manner as with aniline, yielding *benzylidene-o-toluidine*, b. p. 210—212°/72 mm. With dimethylaniline, much heat was developed and a green, resinous product resulted. H. W.

$\alpha\epsilon$ -Dialdehydes and $\alpha\epsilon$ -Keto-aldehydes and their Conversion into δ -Lactones. Constitution and Method of Formation of Amaric Acid, Diethylcarbобензоніс Acid and Allied Compounds. HANS MEERWEIN (*J. pr. Chem.*, 1918, [ii], 97, 225—287).— $\alpha\epsilon$ -Dialdehydes and $\alpha\epsilon$ -keto-aldehydes, of which glutaraldehyde is the only member hitherto known, are easily prepared by the two methods represented by the equations:



Method (1) is new, and noteworthy in that it has hitherto been regarded as impossible to effect the addition of a compound containing a reactive methylene group at the double linking of an $\alpha\beta$ -unsaturated aldehyde; yet in some cases the reaction proceeds with astonishing ease (see below). Satisfactory yields of the additive products are obtained by method (2), despite the well-known sensitiveness of phenylacetaldehyde towards alkali; the conclusion must therefore be drawn that the aldehydo-group causes a greater activation of the methylene hydrogen than does the acetyl or carboalkyloxy-group.

The constitutions of the keto-aldehydes described below are proved by oxidising the substances to the δ -ketonic acids, and all of them except ethyl α -acetyl- γ -aldehydo- β - γ -diphenylbutyrate are converted by alcoholic sodium ethoxide into isomeric δ -lactones by an intramolecular Cannizzaro reaction. The stability of the δ -lactones and of the δ -hydroxy-acids obtained from them differs greatly. The α -mono- and $\alpha\alpha$ -di-alkylated δ -hydroxy-acids are the most stable and lactonise comparatively slowly, and the fission of the corresponding lactones is the most difficult. The lactones almost without exception occur in stereoisomeric forms, which are very easily converted one into another by acids and alkalis. Three of the lactones prove to be the long-known diethylcarbобензоник acid, dipropylcarbобензоник acid, and amaric anhydride, and the mechanism of the formation of these substances is now readily explicable.

The type of additive reaction represented in method (1) suggests a new explanation of the formation of benzanthrone from anthrone, glycerol, and sulphuric acid, depending on the structural similarity of anthrone and deoxybenzoin. Acraldehyde is formed, and this reacts additively with anthrone, producing β -anthronylpropionaldehyde, which passes through dihydrobenzanthrone to benzanthrone.

[With Jos. KLINGZ.]— *β -Phenyl- β -desylpropaldehyde,*
 $\text{COPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHO}$,

needles, m. p. $176\cdot5$ — 177° (when heated slowly, decomp.), obtained with the development of heat by the addition of 1—2 c.c. of concentrated sodium methoxide solution or pyridine or diethylamine to a solution of equal molecular quantities of cinnamaldehyde and deoxybenzoin in methyl alcohol at about 5° , yields β -phenyl- β -desylpropionic (Klingemann's β -dehydroamaric, A., 1893, 589) acid by oxidation with chromic or nitric and glacial acetic acids, and is converted into $\beta\gamma$ -triphenylvalerolactone (Zinin's amaric anhydride) by boiling anhydrous sodium methoxide solution, and into δ -hydroxy- $\beta\gamma$ -triphenylvaleric (α -amaric) acid by aqueous methyl-alcoholic potassium hydroxide at the ordinary temperature, more rapidly by warming. The constitution of β -phenyl- β -desylpropionic acid has been proved by its synthesis. Methyl benzylidenemalonate and deoxybenzoin, condensed as above, yield the additive compound, $\text{COPh}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, needles, m. p. $182\cdot5$ — 183° , which by hydrolysis and loss of carbon dioxide is converted into β -phenyl- β -desylpropionic acid, m. p. 240 — 241° . Klingemann's dehydroamaric anhydride is accordingly the lactone, $\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}$

$\text{CPh}\cdot\text{CPh}-\text{O}$. The reduction of β -phenyl- β -desylpropionic acid by sodium amalgam yields an acid which changes very readily into β -amarolactone, $\text{C}_{23}\text{H}_{20}\text{O}_2$, prismatic needles, m. p. 168 — 170° , from which β -amaric acid, $\text{C}_{23}\text{H}_{22}\text{O}_3$, needles (reconverted into the lactone at 156°), is obtained in the usual way. Since β -amaric acid regenerates β -phenyl- β -desylpropionic acid by oxidation, the α - and β -amaric acids are stereoisomerides.

The substance, $C_{11}H_{18}O_2$, m. p. 168° , obtained by Klingemann by heating α -amarolactone (amaric anhydride) with 25% alcoholic sulphuric acid at 100° (*loc. cit.*), is now found to be a third isomeride, $C_{23}H_{20}O_2$, m. p. 171 – 172° , which is named γ -amarolactone. By oxidation with chromic and acetic acids, it yields an isomeric β -phenyl- β -desylpropionic acid, needles, m. p. 173° , which is much more soluble than the acid, m. p. 240 – 241° , is converted into this by fusion, and is identical with Klingemann's α -dehydro-amaric acid.

The additive compound of deoxybenzoin and α -methyl- β -ethylacraldehyde is an oil, which doubtless consists essentially of β -desyl- α -methylvaleraldehyde, $COPh \cdot CHPh \cdot CHEt \cdot CHMe \cdot CHO$, since it yields β -desyl- α -methyl- n -valeric acid, m. p. 141.5 – 143° , by oxidation. It has not been obtained crystalline, and decomposes completely by distillation in a vacuum. By treatment in concentrated methylalcoholic solution at 30 – 40° with a few c.c. of sodium methoxide solution, it is converted into $\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone, m. p. 152° , which is identical with Zagoumenny's dipropylcarbобензоник acid. The corresponding hydroxy-acid, $C_{20}H_{24}O_3$, forms prismatic needles, m. p. 136 – 137° (decomp.). Zagoumenny's dipropylcarbобензоник acid, m. p. 139° , is shown to be a mixture of the β -acid, m. p. 92 – 93° , and the preceding acid, m. p. 152° , which is called the α -acid. The α -acid is converted into the β -acid by heating with methylalcoholic potassium hydroxide at 160° for five hours. The β -acid is dimorphous, crystallising also in needles, m. p. 95 – 96° . By oxidation with chromic and acetic acids, the α - and β -acids yield respectively β -desyl- α -methyl- n -valeric acid and an isomeric acid, $C_{20}H_{22}O_3$, prismatic needles, m. p. 184.5 – 185° . A third isomeride, needles, m. p. 169 – 171° , is obtained by acidifying a solution of the sodium salt, leaflets, of the β -desyl- α -methyl- n -valeric acid, m. p. 141.5 – 143° . By reduction with sodium amalgam, the acid, m. p. 141.5 – 143° , yields, not α -dipropylcarbобензоник acid, but a mixture of two other stereoisomerides, γ -dipropylcarbобензоник acid [γ -($\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone)], needles, m. p. 82 – 84° , and δ -dipropylcarbобензоник acid [δ -($\gamma\delta$ -diphenyl- α -methyl- β -ethylvalerolactone)], needles, m. p. 134° , softening at 130° , of which the latter is insoluble in light petroleum.

The additive compound of crotonaldehyde and deoxybenzoin is β -desylbutaldehyde, $COPh \cdot CHPh \cdot CHMe \cdot CH_2 \cdot CHO$, which yields β -desyl- n -butyric acid, needles, m. p. 134 – 136° , by oxidation. The latter is converted into an isomeride, m. p. 153.5 – 154.5° , by 2% aqueous sodium hydroxide at 50 – 60° . A synthesis of β -desylbutyric acid, m. p. 134 – 136° , from deoxybenzoin and ethylidenemalonate ester, analogous to that of β -phenyl- β -desylpropionic acid (above), is described. β -Desylbutaldehyde in methylalcoholic solution is transformed by aqueous potassium hydroxide into $\gamma\delta$ -diphenyl- β -methylvalerolactone, m. p. 103 – 104° , which is identical with Zagoumenny's diethylcarbобензоник acid (the α -acid). By oxidation with chromic and acetic acids, the α -acid

yields β -desyl-*n*-butyric acid, m. p. 134—136°, but the latter on reduction yields β -diethylcarbобензоник acid [(β) - $\gamma\delta$ -diphenyl- β -methylvalerolactone], needles, m. p. 144—146°. The oxidation of the β -acid yields the β -desyl-*n*-butyric acid, m. p. 153·5—154·5°, from which it would appear that the β -acid is formed by the reduction (by sodium amalgam), not of the β -desyl-*n*-butyric acid, m. p. 134—136°, but of the isomeric acid, m. p. 153·5—154·5°, so easily obtained from it by the action of alkali hydroxide.

Deoxybenzoin and acraldehyde react additively in methyl-alcoholic solution containing a little sodium methoxide to form β -desylpropaldehyde, which yields β -desylpropionic acid by oxidation. The aldehyde cannot be transformed by alkali into $\gamma\delta$ -diphenylvalerolactone, $C_{17}H_{16}O_2$, needles, m. p. 113—114°, which is obtained, however, by the reduction of β -desylpropionic acid by sodium amalgam.

[With HANS DOTT.]—The additive reaction between phenylacetaldehyde and cinnamaldehyde in cold methyl-alcoholic sodium methoxide solution yields $\alpha\beta$ -diphenylglutardialdehyde. This has not been isolated from the solution, but converted by heating on the water-bath into $\beta\gamma$ -diphenylvalerolactone, prisms or needles, m. p. 123—123·5°, together with a small quantity of a substance, m. p. 134—136°, leaflets, which is possibly $\alpha\beta$ -diphenylvalerolactone. By oxidation with alkaline permanganate, $\beta\gamma$ -diphenylvalerolactone yields $\alpha\beta$ -diphenylglutaric acid, prisms, m. p. 203—204° (methyl ester, needles, m. p. 84—85°), which is converted by prolonged fusion into a stereoisomeride (methyl ester, prisms, m. p. 143°), m. p. between 215° and 232°, according to the rate of heating. For this isomeride Borsche found m. p. 230—231° (A., 1910, i, 35), and Avery and McDole m. p. 223—224° (A., 1908, i, 343). By reduction with hydriodic acid (D 1·7) and red phosphorus at 170°, $\beta\gamma$ -diphenylvalerolactone yields $\beta\gamma$ -diphenyl-*n*-valeric acid, prismatic needles, m. p. 109°, the constitution of which follows by exclusion, since the acid is not identical with either of the stereoisomeric forms of $\alpha\beta$ -diphenylvaleric acid.

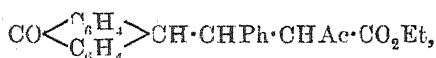
δ -Keto- $\alpha\beta\delta$ -triphenyl-*n*-valeraldehyde, obtained additively from phenylacetaldehyde and phenyl styryl ketone, has also not been isolated, but has been converted through $\alpha\beta\delta$ -triphenylvalerolactone into δ -hydroxy- $\alpha\beta\delta$ -triphenylvaleric acid, needles, m. p. 143—143·5°, which is a remarkably stable acid, but is converted into $\alpha\beta\delta$ -triphenylvalerolactone, needles, m. p. 138—139°, by heating in a vacuum at 150°. The acid is oxidised by chromic acid or potassium permanganate, although not smoothly, to δ -keto- $\alpha\beta\delta$ -triphenylvaleric acid, which is best isolated as the methyl ester, $C_{24}H_{22}O_3$, needles, m. p. 157—158°. The acid, felted needles, m. p. 186—187°, has been obtained by hydrolysing the ester and also synthetically from phenyl styryl ketone and methyl phenylacetate. A second isomeric acid is also obtained by the synthetic method, which has m. p. 260—261°, forms a methyl ester, needles, m. p. 177—178°, and is also obtained by heating the acid, m. p. 186—

187°, at 200—220°. $\alpha\beta\delta$ -Triphenylvalerolactone is reduced to $\alpha\beta\delta$ -triphenylvaleric acid, m. p. 174—175°, by hydriodic acid (D 1·7) and red phosphorus at 170°, and is converted by warm glacial acetic acid containing 10% of sulphuric acid into a *stereoisomeride*, $C_{23}H_{20}O_2$, prisms with $1C_2H_4O_2$, m. p. 124° (174° after removal of acetic acid), from which is obtained a δ -hydroxy- $\alpha\beta\delta$ -triphenylvaleric acid, prisms with $1EtOH$, m. p. 155° (not sharp), with reconversion into the lactone.

Phenylacetaldehyde and ethyl benzylideneacetoacetate react additively in alcoholic solution at 5° in the presence of a little sodium ethoxide to form δ -keto- γ -carbethoxy- $\alpha\beta$ -diphenyltheraldehyde, $CHO \cdot CHPh \cdot CHPh \cdot CHAc \cdot CO_2Et$, rhombic leaflets containing $1H_2O$, m. p. 149° (decomp.), and a substance, $C_{23}H_{20}O_5$, prisms, m. p. 79—81°. This substance, the constitution of which has not yet been determined, is also formed by treating the aldehyde with 5% alcoholic hydrogen chloride; it is converted by distillation in a vacuum into an unsaturated substance, $C_{23}H_{26}O_4$, needles, m. p. 129—130°. The preceding aldehyde, which is a viscous oil in the anhydrous state, is converted by distillation in a vacuum into ethyl acetoacetate and α -phenylcinnamaldehyde, crystals, m. p. 94° (orime, leaflets, m. p. 165—166°; phenylhydratone, yellow needles, m. p. 125—126°), which has also been synthesised from phenylacetaldehyde and benzaldehyde by Claisen's method.

[With Jos. KLINZ.]—Methyl β -anthronyl- β -phenylisosuccinate, $CO \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot CHPh \cdot CH(CO_2Me)_2$, prisms, m. p. 147°, prepared by adding a few drops of piperidine or diethylamine to a warm methyl-alcoholic solution of anthrone and methyl benzylidene-malonate, is converted into β -anthronyl- β -phenylpropionic acid, prisms, m. p. 195—197° (rapidly heated; decomp. by slow heating), by hydrolysis with boiling 30% sulphuric and glacial acetic acids for four to five days.

By similar additive reactions, anthrone unites with ethyl benzylideneacetoacetate and with phenyl styryl ketone to form ethyl α -acetyl- β -anthronyl- β -phenylpropionate,



needles, m. p. 148—149°, and phenyl β -anthronyl- β -phenylethyl ketone, $CO \langle \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} \rangle CH \cdot CHPh \cdot CH_2 \cdot CPh$, needles, m. p. 115—116°, respectively.

C. S.

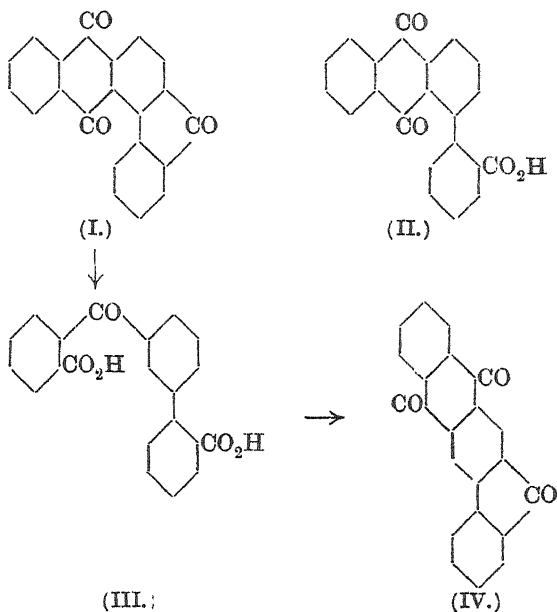
Action of Potassium Ferricyanide on Alizarin in Alkaline Solution and Constitution of Salts of Hydroxyanthraquinones. ROLAND SCHOLL and A. ZINKE (*Ber.*, 1918, 51, 1419—1435).—By oxidation with an aqueous solution of potassium

ferricyanide and potassium hydroxide at the ordinary temperature, alizarin is converted into an *acid*, $C_{14}H_8O_6$, hydrated, yellow leaflets, m. p. about 230° (decomp.; darkening above 150°), which is purified through the *calcium* salt, and the *monoethyl* ester, yellow or brownish-yellow crystals, m. p. 149° , or *diethyl* esters, yellow plates, prisms, or needles, m. p. $85.5-87^\circ$, and yellow, prismatic needles, m. p. 188° (probably *cis-trans*-isomerides). The acid is shown to be *2-hydroxy-1:4-naphthaquinone-3-vinylglyoxylic acid*, $OH \cdot C_{10}H_4O_2 \cdot CH:CH \cdot CO \cdot CO_2H$, by the following evidence. It acts as a dibasic acid, forming a calcium salt, $C_{14}H_6O_6Ca$, which exists in four forms, violet-brown crystals with $7H_2O$, blackish-violet crystals with $3H_2O$, blackish-violet salt with $1H_2O$, and bronze, rhombic leaflets with $2H_2O$, and a *dipotassium* salt, $C_{14}H_6O_6K_2$, brown crystals with $2H_2O$. It forms a vat with alkaline hypsulphite, and therefore contains a quinone grouping. It can be converted into a naphthafuranquinone, and is therefore a naphthaquinone derivative. The monoethyl ester gives a violet-red coloration with alcoholic ferric chloride. The acid reacts additively with bromine.

The views of Perkin (T., 1899, 75, 433; 1903, 83, 129), von Georgievics (A., 1902, i, 635; 1905, i, 447), Werner (A., 1908, i, 440), Pfeiffer (A., 1913, i, 879), and Dimroth (*Annalen*, 1916, 411, 340) on the constitution of hydroxyanthraquinones in the form of their salts and the nature of mordant dyes are discussed without any very definite conclusion being reached. C. S.

Rearrangement Reactions in the Anthraquinonefluorenone Series. ALFRED SCHAARSCHMIDT and JOHANN HERZENBERG (*Ber.*, 1918, 51, 1230-1237).—1-Chloroanthraquinone-2-carboxylic acid is converted by boiling with toluene and phosphorus pentachloride into the acid *chloride*, pale yellow needles, a suspension of which in benzene is converted into 1-chloro-2-benzoylanthraquinone, $C_{20}H_{11}O_3Cl$, yellow leaflets, m. p. 196° , by heating with aluminium chloride at 60° for four hours. 1-Amino-2-benzoylanthraquinone, red needles, m. p. 190° , prepared by heating the preceding substance with alcohol and aqueous ammonia at $170-175^\circ$, is diazotised in concentrated sulphuric acid solution at $17-22^\circ$, the solution is poured on to ice so that the temperature does not exceed about 35° , copper powder is added, and the mixture warmed on the water-bath, whereby anthraquinone-2:1-fluorenone (formula I), golden-yellow leaflets (from nitrobenzene), m. p. 317° , is obtained, which forms an intensely red vat with sodium hyposulphite. By fusion with potassium hydroxide at $220-230^\circ$, anthraquinone-2:1-fluorenone is converted, not into 1-o-carboxyphenylantraquinone (formula II) as might be expected from the behaviour of allochrysoketonecarboxylic acid (Schaarschmidt, A., 1917, i, 274), but into a mixture of acids containing the dicarboxylic acid (formula III), since by treatment with concentrated sulphuric

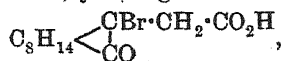
acid, Ullmann and Dasgupta's anthraquinone-2:3-fluorenone (A., 1914, i, 413) was obtained (formula IV).



C. S.

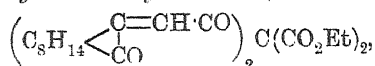
Camphor Ketones. HANS RUPE, MARKUS WARDER, and KUNIIKO TAKAGI (*Helv. Chim. Acta*, 1918, i, 309—342).—The work of Rupe and Iselin (A., 1916, i, 409) and of Rupe and Burckhardt (A., 1917, i, 141) on the preparation of derivatives of methylenecamphor has been extended in several directions, particularly with a view to the preparation of an unsaturated camphor ketone; the optical investigation of the substances is not yet quite completed, and fuller details are promised in a subsequent communication.

Camphorylideneacetic acid, $C_8H_{14} \begin{smallmatrix} \diagup C=CH \cdot CO_2H \\ \diagdown CO \end{smallmatrix}$, m. p. 99.5—101°, $[\alpha]_D + 182.3^\circ$ in benzene, is prepared by a modification of the method of Bishop, Claisen, and Sinclair (A., 1895, i, 62) [the microcrystalline *magnesium* salt and the ethyl ester, pale yellow, inodorous oil, b. p. 149.5—150°/12 mm., $D_4^{20} 1.0459$, $[\alpha]_D + 170.1^\circ$ (in substance), +160.4 (in benzene), are described], and is converted by thionyl chloride into the corresponding *chloride*, m. p. 34—35°, b. p. 140—141°/13 mm. The free acid reacts with hydrogen bromide in glacial acetic acid solution, yielding the bromo-acid,



long, colourless needles, m. p. 153—154° (decomp.), but the action appears to be balanced, since, at a slightly higher temperature, hydrogen bromide is eliminated with re-formation of camphorylideneacetic acid. The latter substance does not react normally with bromine. *Camphorylacetic acid*, small, prismatic crystals, m. p. 83—84°, b. p. 191·5—192·5°/12 mm., $[\alpha]_D + 38\cdot0$ in benzene, is prepared by reducing camphorylideneacetic acid with sodium amalgam, or, better, with hydrogen, in the presence of nickel; its *ethyl ester* has b. p. 154—155°/10 mm., $[\alpha]_D + 67\cdot5^\circ$ (in substance), $+ 37\cdot1^\circ$ (in benzene). Attempts to reduce camphorylideneacetyl chloride by zinc dust and acetic acid led to the isolation of a mixed *anhydride* of camphorylacetic and acetic acids, $C_8H_{14} \begin{smallmatrix} \text{CH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{Ac} \\ \text{CO} \end{smallmatrix}$, fine needles or transparent plates, m. p. 118—120°.

Ethyl dicamphorylideneacetylmalonate,



pale yellow needles, m. p. 90—91°, is prepared by the condensation of camphorylideneacetyl chloride with ethyl sodiomalonate in ethereal solution (*ethyl dicamphorylideneacetylacetate*, fine needles, m. p. 149—150°, is similarly obtained from ethyl acetoacetate), and is hydrolysed by dilute sulphuric acid in acetic acid solution to *camphorylideneacetone*, $C_8H_{14} \begin{smallmatrix} \text{O}=\text{CH}\cdot\text{CO}\cdot\text{CH}_3 \\ \text{CO} \end{smallmatrix}$, lemon-

yellow liquid, b. p. 137—138°/10 mm., $D_4^{20} 1\cdot0327$, $[\alpha]_D + 208\cdot8^\circ$ (in substance), $186\cdot6^\circ$ (in benzene), and camphorylideneacetic acid. The ketone does not appear to yield a stable sodium hydrogen sulphite compound; the *benzylidene* derivative forms golden-yellow needles, m. p. 94—95°, *p-nitrobenzylidene* derivative, lemon-yellow, minute crystals, m. p. 150—151°, *oxime*, colourless, shining needles, m. p. 142—143°, *phenylhydrazone*, orange-yellow needles, m. p. 145—146°, *hydrazone*, long, yellow needles, m. p. 112—113°. With semicarbazide the ketone gives a *compound*, $C_{14}H_{21}O_5N_3$, prismatic needles or small leaflets, decomposing at 223—224°, which does not behave as a normal semicarbazone.

Attempts to prepare *camphorylaceton* by a similar sequence of actions were less successful. *Camphorylacetyl chloride*, pale yellow, inodorous liquid, b. p. 152—154°/12 mm., could only be condensed with ethyl sodiomalonate with considerable difficulty, giving a small yield of substance, from which by hydrolysis camphorylaceton was obtained in small quantity. The saturated ketone could, however, be satisfactorily prepared by reduction of camphorylideneacetone with hydrogen in the presence of nickel, although the camphor carbonyl group was invariably attacked to some extent; after purification through the *semicarbazone*, long needles, m. p. 203—204° (decomp.), it was obtained as an inodorous, highly refractive oil, b. p. 148·5—149°/12 mm., $D_4^{20} 1\cdot0213$, $[\alpha]_D + 49\cdot2^\circ$ (in substance), $+ 60\cdot7^\circ$ (in benzene). The ketone behaves towards sodium hydrogen sulphite in the same manner as the unsaturated ketone; it yields a

phenylhydrazone, needles, m. p. 87—89°, and a *benzylidene* derivative, colourless leaflets, m. p. 75—76°.

The preparation of a camphordiketone is also described, although the yields leave much to be desired in spite of many variations of the experimental conditions; ethyl camphorylacetate condenses with acetophenone in ethereal solution in the presence of solid sodium ethoxide, giving small amounts of *camphorylacetylacetophenone*, $C_8H_{14} \begin{smallmatrix} < \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COPh} \end{smallmatrix}$, m. p. 59—61°, $[\alpha]_D + 62.5^\circ$ in

benzene. An alcoholic solution of the diketone gives an immediate bluish-red coloration with ferric chloride. The *copper* salt, long, greyish-green needles, m. p. 184—186°, and *sodium* salt are described. H. W.

Preparation of Camphylcarbinol. HANS RUPE (D.R.-P. 307357; from *Chem. Zentr.*, 1918, ii, 493).—Hydroxymethylenecamphor only suffers reduction at the ethylenic bond when reduced by hydrogen in the presence of finely divided nickel or cobalt in alcoholic, aqueous-alcoholic, or acetic acid solution, or as normal alkali salt in aqueous solution; *camphylcarbinol*, which is thus produced, is a colourless, odourless oil, b. p. 142—143°/10 mm., D_4^{20} 1.0502, $[\alpha]_D^{20} + 62.22^\circ$. [See further, following abstract.] H. W.

Reduction Products of Hydroxymethylenecamphor. H. RUPE, A. AKERMANN, and H. TAKAGI (*Helv. Chim. Acta.*, 1918, 1, 452—472).—The reduction of hydroxymethylene compounds by hydrogen in the presence of colloidal palladium or platinum has been studied by Kötze and Schaeffer (A., 1912, i, 603), who found that methyl ketones were formed; hydroxymethylenecamphor, however, was unaffected by this treatment, a result which was attributed to the acidic character of the substance. The authors find that hydroxymethylenecamphor is readily reduced by hydrogen in the presence of a specially prepared nickel catalyst (the mode of procedure is fully described in the original paper and iron and copper are shown to act as poisons). The main product (about 80—95%) of the reaction is *camphylcarbinol*, $C_8H_{14} \begin{smallmatrix} < \\ \text{CO} \end{smallmatrix} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{smallmatrix}$; it is purified by repeated fractionation under diminished pressure, or, preferably, by means of the calcium chloride compound; the optically pure substance is isolated through the benzoyl derivative (see later). It forms a colourless, odourless, viscous oil, b. p. 139—140°/9 mm., 143—144°/11 mm., D_4^{20} 1.0502, $[\alpha]_D^{20} + 49.13^\circ$, $[\alpha]_B^{20} + 65.73^\circ$, $[\alpha]_E^{20} + 82.44^\circ$, $[\alpha]_F^{20} + 120.82^\circ$, $[\alpha]_F/[\alpha]_C$ 2.45°, λ_D 578. With phosphorus tribromide it yields the corresponding *bromide*, long needles, m. p. 65.5—66°, and with hydrogen chloride, or, preferably, thionyl chloride, the corresponding *chloride*, leaflets, m. p. 53—54°, b. p. 125—127°/14 mm. Attempts to convert the alcohol into the aldehyde were unsuccessful; chromic oxide converted it into camphorquinone, m. p. 197°, whilst manganese dioxide and sulphuric

acid gave a small quantity of substance, m. p. 201° , and much unchanged carbinol. Benzoyl chloride in the presence of pyridine converts the carbinol practically quantitatively into the *benzoyl* derivative, colourless, shining plates or prisms, m. p. $95-97^{\circ}$; attempts to hydrolyse the latter with alcoholic potassium hydroxide, with barium hydroxide, or magnesia resulted in the formation of methylenecamphor. Experiments with aqueous alcoholic sulphuric acid were more successful, and from these it was found possible to isolate camphylcarbinol, although dehydration of the latter also occurred to a considerable extent. The *formyl* derivative, long needles, m. p. $74-75^{\circ}$, b. p. $142-143^{\circ}/11$ mm., and the *acetyl* derivative, colourless, mobile oil, b. p. $148.5-149^{\circ}/10$ mm., were prepared by the action of formic acid (86%) and acetic anhydride respectively on the carbinol, but attempts to prepare the hydrogen phthalate led to the production of methylenecamphor.

The by-products of the preparation of camphylcarbinol consist of methylenecamphor, methylcamphor, and the ethyl ethers of camphylcarbinol and hydroxymethylenecamphor. The two substances first named are contained in the first fractions, b. p. *ca.* $82-84^{\circ}/10$ mm., and are separated by converting the methylenecamphor into the hydrobromide (camphylbromomethane), from which it can be re-generated by treatment with methyl-alcoholic potassium hydroxide; the pure substance is, however, more conveniently prepared by heating camphylcarbinol with the same reagent, and then forms a characteristic, waxy mass, m. p. $43.5-44^{\circ}$. It becomes polymerised when repeatedly distilled under diminished pressure. With bromine it yields a *dibromide*, m. p. $108-109^{\circ}$. *Methylcamphor*,

$\text{C}_8\text{H}_{14} \begin{array}{l} \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$, can be isolated in an almost pure state by repeated fractionation of the residues from the methylenecamphor hydrobromide, but is more conveniently obtained by the direct hydrogenation of methylenecamphor in the presence of finely divided nickel; it has m. p. $37.5-38.5^{\circ}$, b. p. $88-89^{\circ}/8.5$ mm. Direct experiment shows the formation of methylenecamphor to be due to the dehydrating action of the nickel catalyst on primarily formed camphylcarbinol.

The ethyl ethers of camphylcarbinol and hydroxymethylenecamphor were not isolated as such; their presence is inferred from the fact that the action of alcoholic potassium hydroxide on the fractions of higher b. p. of the by-products leads to the production of methylenecamphor and hydroxymethylenecamphor respectively; their formation is attributed to the addition of ethyl alcohol to methylenecamphor and to the condensation of hydroxymethylenecamphor and alcohol under the influence of nickel. H. W.

Synthesis of Curcumin. V. LAMPE (*Ber.*, 1918, 51, 1347-1355).—The course of the synthesis is as follows: ethyl α -carbomethoxyferuloylacetoacetate \rightarrow carbomethoxyferuloylacetone \rightarrow dicarbomethoxydiferuloylacetone \rightarrow dicarbomethoxydiferuloylmethane \rightarrow diferuloylmethane (curcumin).

Ethyl α-carbomethoxyferuloylacetoacetate [*ethyl α-4-methylcarbonato-3-methoxycinnamoylacetoacetate*],

$\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, obtained by digesting ethyl sodioacetoacetate and carbomethoxyferuloyl [4-methylcarbonato-3-methoxycinnamoyl] chloride in dry ether on the water-bath, forms faintly yellow needles, m. p. 91—93°; a by-product of the reaction is *methyl carbonatomethoxycinnamic anhydride*, $\text{C}_{24}\text{H}_{22}\text{O}_{11}$, colourless leaflets, m. p. 142—144°. *Ethyl α-feruloylacetoacetate*, $\text{C}_{16}\text{H}_{18}\text{O}_6$, canary-yellow, prismatic needles, m. p. 116—118°, is obtained by shaking an ethereal solution of the methyl carbonato-derivative with 1% aqueous sodium hydroxide and treating the alkaline solution with carbon dioxide.

Carbomethoxyferuloylacetone [4-methylcarbonato-3-methoxycinnamoylacetone], $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COMe}$, faintly yellow, prismatic needles, m. p. 111—113°, is obtained by hydrolysing ethyl α-methylcarbonatomethoxycinnamoylacetoacetate, carbon dioxide being also eliminated; it is converted into *feruloylacetone*, $\text{C}_{13}\text{H}_{14}\text{O}_4$, prisms, m. p. 143—145°, by dilute alkali.

A solution of methylcarbonatomethoxycinnamoylacetone in anisole is treated with finely divided sodium, and a day later a solution of methylcarbonatomethoxycinnamoyl chloride in warm anisole is added. The mixture is treated after twenty-four hours with water containing a little hydrochloric acid, and the anisole is removed by distillation with steam. The heavy, dark red residue, probably dimethylcarbonatomethoxydicinnamoylacetone, is boiled with dilute acetic acid, and thus converted into dimethylcarbonatomethoxydicinnamoylmethane, m. p. 145—148—158°; after crystallisation from benzene the substance is pure, has m. p. 170—172°, and is identical with Milobendzka, Kostanecki, and Lampe's dimethylcarbonato-curcumin (A., 1910, i, 628); the last substance has m. p. 170—172° after being crystallised from benzene. On hydrolysis dimethylcarbonatomethoxydicinnamoylmethane yields diferuloylmethane, $\text{CH}_2(\text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3[\text{OMe}] \cdot \text{OH})_2$, prisms, m. p. 180—183°, which is identical with natural curcumin. C. S.

Synthesis of *pp'*-Dihydroxy- and *p*-Hydroxydicinnamoylmethane. V. LAMPE and M. GODLEWSKA (*Ber.*, 1918, 51, 1355—1360).—The method of synthesising dicinnamoylmethane (Lampe and Milobedzka, A., 1913, i, 876) has been extended to include the hydroxy-derivatives, partly in connexion with the synthesis of curcumin (preceding abstract), partly to obtain substances which are of interest in connexion with the theory of direct dyes.

The condensation of ethyl acetoacetate and *p*-methylcarbonatocinnamoyl chloride in ethereal solution by means of sodium ethoxide yields, in addition to a little *p*-methylcarbonatocinnamic anhydride, $\text{C}_{22}\text{H}_{18}\text{O}_9$, colourless aggregates, m. p. 168—170°, *ethyl α-p-methylcarbonatocinnamoylacetoacetate*,

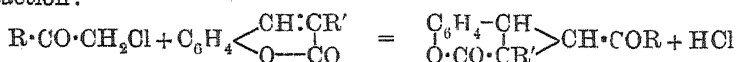
$\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{CHAc} \cdot \text{CO}_2\text{Et}$, faintly yellow prisms, m. p. 94—96°, which yields by hydrolysis and simultaneous elimination of carbon dioxide *p*-methylcarbonatocin-

namoylacetone, $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COMe}$, faintly yellow leaflets, m. p. 111—113°. The last compound reacts in ethereal solution with very dilute alkali to form *p*-hydroxycinnamoylacetone, yellow leaflets, m. p. 144—146°, in boiling alcoholic solution with hydroxylamine hydrochloride to form 3(or 5)-*p*-methylcarbonatostyryl-5(or 3)-methylisooxazole, $\text{C}_{14}\text{H}_{13}\text{O}_4\text{N}$, colourless leaflets, m. p. 122—124°, and in anisole solution with sodium and *p*-methylcarbonatocinnamoyl chloride to form, after the initial product has been boiled with dilute acetic acid (compare preceding abstract), *pp'*-dimethylcarbonatodicinnamoylmethane, $\text{C}_{22}\text{H}_{20}\text{O}_8$, canary-yellow aggregates, m. p. 162—166°. The last substance reacts with hydroxylamine hydrochloride in alcoholic solution to form 3:5-di-*p*-methylcarbonatostyrylisooxazole, $\text{C}_{23}\text{H}_{19}\text{O}_7\text{N}$, colourless aggregates, m. p. 178—180°, and in ethereal solution with 1% aqueous sodium hydroxide to form *pp'*-dihydroxydicinnamoylmethane, $\text{C}_{19}\text{H}_{16}\text{O}_4$, faintly orange needles, m. p. 218—220° (decomp.).

p-Methylcarbonatodicinnamoylmethane, $\text{C}_{21}\text{H}_{18}\text{O}_5$, yellow needles, m. p. 114—116°, is obtained from cinnamoylacetone and *p*-methylcarbonatocinnamoyl chloride or *p*-methylcarbonatocinnamoylacetone and cinnamoyl chloride by the aid of sodium and acetic acid (as above), and yields by elimination of the carbomethoxy-group *p*-hydroxydicinnamoylmethane, faintly orange, prismatic needles, m. p. 190—192°.

Unmordanted cotton is dyed faintly orange by curcumin, canary-yellow (not fast to soap) by *pp'*-dihydroxydicinnamoylmethane, and faintly yellow by *p*-hydroxydicinnamoylmethane. A similar regularity occurs in the reaction with boric acid, which colours turmeric (curcumin) paper intensely orange, changes the colour of *pp'*-dihydroxydicinnamoylmethane to a weak orange, and does not affect the colour of *p*-hydroxydicinnamoylmethane. C. S.

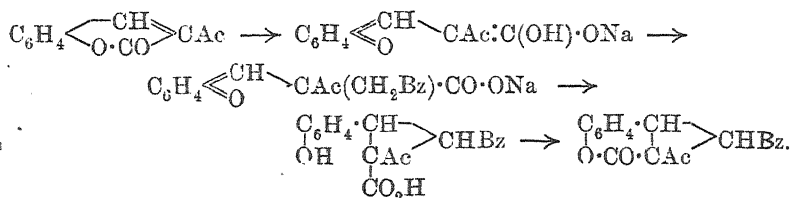
A New Group of cycloPropane Derivatives. III. Scope and Mechanism of the Reaction. Behaviour of 3-Acetylcoumarin with Solutions of Alkali Hydroxides. OSKAR WIDMAN (*Ber.*, 1918, 51, 1210—1214. Compare A., 1918, i, 347, 393).—The formation of the new cyclopropane derivatives by the reaction:



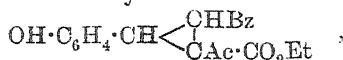
(*loc. cit.*) succeeds when $\text{R} = \text{Ph}$, *o*- or *p*- $\text{C}_6\text{H}_4\cdot\text{OMe}$, $\text{C}_6\text{H}_4\cdot\text{NO}_2$, or C_{10}H_7 , and $\text{R}' = \text{Ac}$, COEt , Bz , CO_2Et , CO_2Me , or CN , but fails when $\text{R} = \text{Me}$ and $\text{R}' = \text{Ph}$ or H . The formation also fails when ethyl coumarin-4-carboxylate is used instead of a suitably 3-substituted coumarin. Attempts also failed to bring about, in the presence of sodium ethoxide, a reaction between phenacyl haloids and esters of fumaric, ethylenetetracarboxylic, benzylideneacetoacetic, benzylidenemalonic, anisylidenemalonic, and *o*-ethoxybenzylideneacetoacetic acids in such a way that the phenacylidene group is combined at a double linking. It appears, therefore, that only 3-substituted coumarins can enter into the preceding reaction, and even then only

if the substituent is an aliphatic or aromatic acyl group, a carbo-alkyloxy-group, or a cyano-group.

In seeking to account for the reaction, the author has revised his explanation of the action of alkalis on 3-acetylcoumarin (A., 1902, i, 374). The yellow colour developed with a cold solution of alkali hydroxide is now attributed, not to the formation of 3-hydroxyvinyl-coumarin, because 3-trimethylacetyl- and 3-benzoyl-coumarin, in which the formation of the hydroxyvinyl group is impossible, also develop a yellow colour, but to the formation of an orthoquinonoid sodium compound. This reacts with the phenacyl haloid in accordance with the scheme:



When alcoholic sodium ethoxide is used a certain amount of the substance $\text{O}:\text{C}_6\text{H}_4:\text{CH}:\text{CAc}:\text{C}(\text{OEt})\cdot\text{ONa}$ is formed, and this reacts with the phenacyl haloid to yield the coumarinic ester,



and thus is explained the formation of a by-product differing from the main product in containing an additional molecule of ethyl alcohol (*loc. cit.*). C. S.

A Synthesis of *iso*Brazilein and certain Related Anhydro-pyranol Salts. I. HERBERT GRACE CRABTREE, ROBERT ROBINSON, and MAURICE RUSSELL TURNER (T., 1918, 113, 859—880).

Preparation of Hydrogenated Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P., 307894; additional to D.R.-P., 306939; from *Chem. Zentr.*, 1918, ii, 693—694).—The addition of hydrogen to alkaloids or their salts in the presence of small quantities of the finely divided suboxides of the nickel group (A., 1918, i, 546) at temperatures not exceeding 60° can also be effected in alcoholic suspension or solution. The preparation of dihydroquinine from quinine monohydrochloride and the hydrogenation of cinnamyl-cocaine are cited as examples. H. W.

Cinchona Alkaloids. I. Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1918, 51, 1325—1333).—Contrary to the statement of Hesse (A., 1888, 71), dihydrocupreine instantly decolorises potassium permanganate in acid solution. It has m. p. 204° (Hesse gives 168—170°; Pum, 170°), and can readily be obtained by the addition of hydrogen to cupreine in alcoholic solution (palladium catalyst) or to cupreine hydrochloride in aqueous solution (nickel catalyst).

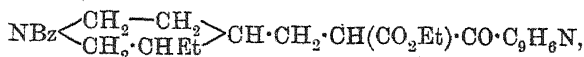
Cupreine yields methylcupreine (quinine) by methylation with methyl sulphate and alkali in methyl-alcoholic solution, or, much better, with ethereal diazomethane in amyl-alcoholic solution.

Methyldihydrocupreine, prepared by the catalytic reduction of quinine or the methylation of dihydrocupreine, is isolated as the *basic sulphate*, which contains $6\text{H}_2\text{O}$ and is relatively stable to potassium permanganate. Ethyldihydrocupreine is prepared by similar methods. C. S.

The Cinchona Alkaloids. XX. Synthesis of Quinotoxines.

PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 1360—1365. Compare A., 1918, i, 303).—The problem of the synthesis of quinotoxines resolves itself into three parts: (1) the synthesis of cinchoninic and 6-methoxycinchoninic acids, (2) the synthesis of homomeroquinene and homocincholeupone, and (3) the condensation of each of the first with each of the second pair to give the four quinotoxines, cinchonidine, dihydrocinchonidine, quinidine, and dihydroquinidine.

The first part will be dealt with in a later communication by Rabe. With regard to the second part, the two substances have not yet been synthesised, and the material used by the authors in realising the third part has been obtained by the fission of quinotoxines. Thus *N*-benzoylhomocincholeupone, obtained from benzoyldihydrocinchotoxine by a slight modification of Kaufmann and Brunnschweiler's method (A., 1917, i, 50), is converted into its *ethyl* ester, $\text{C}_{19}\text{H}_{27}\text{O}_3\text{N}$, a viscous oil, b. p. $256^\circ/13$ mm., which yields, after hydrolysis by dilute hydrochloric acid and subsequent re-esterification, *ethyl homocincholeupone*, $\text{C}_{12}\text{H}_{23}\text{O}_2\text{N}$, b. p. $140^\circ/13$ mm. The reaction between ethyl cinchoninate and ethyl *N*-benzoylhomocincholeupone in the presence of sodium ethoxide in boiling benzene for fifteen hours leads to a product, doubtless the β -ketonic ester,

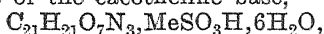


which is converted into dihydrocinchotoxine (dihydrocinchonidine) by hydrolysis with boiling 15% hydrochloric acid.

Since dihydrocinchotoxine can be converted into dihydrocinchoninone (A., 1909, i, 253), and the latter has been reduced by aluminium and sodium ethoxide to dihydrocinchonine and dihydrocinchonidine (future communication), therefore the construction of cinchona alkaloids from derivatives of the quinoline and piperidine series has been accomplished. C. S.

Degradation of Scopoline. ERNST SCHMIDT (*Ber.*, 1918, **51**, 1281—1283).—A claim for priority over Hess with respect to the conversion of dihydroscopoline into 1-methylpiperidine-2:6-dicarboxylic acid, and a denial of his statement (A., 1918, i, 404) that the author has asserted that the group $\text{O} \left\langle \begin{array}{c} \text{C}(\text{OH}) \\ \text{CH} \end{array} \right\rangle$ is present in scopoline. C. S.

Strychnine Alkaloids. XXIV. Cause of the Violet Colour Reaction of Cacotheline and of Nitro-compounds of the Brucine Series Allied to it. HERMANN LEUCHS (*Ber.*, 1918, 51, 1375—1389).—The action of nitric acid on brucine is represented by the scheme $C_{23}H_{26}O_4N_2 \rightarrow C_{21}H_{20}O_4N_2 \rightarrow C_{21}H_{19}O_6N_3 \rightarrow C_{21}H_{21}O_7N_3.HNO_3$ (A., 1911, i, 746). Cacotheline, the final product, would appear to be a nitrated quinone were it not that sulphurous acid does not produce a less intensely coloured or colourless quinol (A., 1910, i, 1042), but a substance having a deep violet or deep green colour. Brucinolone and isobrucinolone when treated with nitric acid undergo analogous changes (A., 1909, i, 954; 1912, i, 210; 1913, i, 194), the final product being undoubtedly a nitro-quinone, since it is reduced by sulphurous acid to a pale yellow quinol. Hence by analogy the cacotheline base is a nitro-quinone, despite the objection raised above. The same holds in the case of the methonitrate of the cacotheline base, $C_{21}H_{21}O_7N_3.MeNO_3$, obtained by the action of nitric acid on methylbrucine (A., 1911, i, 1018). The methonitrate also gives a violet coloration with sulphurous acid, but its quinonoid nature is shown first by the reaction with aqueous hydroxylamine hydrochloride, whereby the *oxime*, $C_{22}H_{25}O_7N_4Cl.2H_2O$, yellow needles, of the methochloride of the cacotheline base is obtained, and, secondly, by reduction by tin and *N*-hydrochloric acid, whereby four atoms of hydrogen are taken up and a *stannichloride*, broad, rectangular prisms, is obtained, $C_{22}H_{29}O_5N_3Cl.HCl.SnCl_4.6H_2O$, from which the *hydrochloride* of presumably an amino-quinol, $C_{22}H_{29}O_5N_3Cl.HCl.H_2O$, colourless, crystalline powder, decomp. 260° , is prepared. The behaviour of the methonitrate towards sulphurous acid is at variance with the preceding evidence of quinonoid structure. Thus with aqueous sodium hydrogen sulphite it yields, in the cold at 0° , a *methosulphite* of the cacotheline base,



colourless leaflets, which evolves sulphur dioxide on treatment with strong acids, and in the hot solution an isomeric *methosulphite*, deep violet, almost black prisms with metallic lustre (into which the colourless isomeride changes by keeping), which dissolves in concentrated sulphuric acid without evolution of sulphur dioxide, and is precipitated unchanged by the addition of water. Probably, therefore, the sulphurous acid in the violet compound is not only attached to the basic nitrogen atom, but also enters into complex combination with some other portion of the molecule. By treatment with 5*N*-nitric acid, the violet compound loses two atoms of hydrogen and is converted into a *substance*, $C_{21}H_{19}O_7N_3.MeSO_3H$, reddish-yellow leaflets or prisms with $2H_2O$, which appears to bear to the violet compound the relation of quinone to quinol, since it is converted into the latter by sulphurous acid or by nickel and hydrochloric acid. Hydroxylamine, however, converts the reddish-yellow substance into the violet compound in acid solution and into the oxime of the methochloride of the cacotheline base in alkaline solution. The complete reduction of the reddish-yellow

substance by tin and hydrochloric acid yields at first a violet precipitate, and, finally, a substance, $C_{22}H_{25}O_7N_3S$, colourless needles, which appears to be the anhydride resulting by the elimination of water from an amino- and the SO_3H -groups. The SO_2 group is still present in complex union in the anhydride, but is eliminated by warm *N*-alkali hydroxide, without, however, definite products being formed.

The violet compound, $C_{21}H_{21}O_7N_3MeSO_3H$, is stable in aqueous ammonia in the absence of oxygen, but when the latter is admitted is oxidised, to the extent of 10% to the reddish-yellow nitro-quinone methosulphite and to the extent of 60% to a substance, $C_{21}H_{23}O_{11}N_3S$, reddish-yellow prisms and polyhedra, carbonising at about $280-290^\circ$.

Apart from their acidic groups, the methonitrate of the cacotheline base, and the violet methosulphite obtained from it by the action of sodium hydrogen sulphite, are isomeric substances. The former is a nitro-quinone and the latter a nitro-quinol. The reduction of the one to the other is not effected at the expense of the sulphurous acid, because the two substances are isomeric. The author is of opinion that intramolecular reduction occurs at the expense of a $\cdot CH(OH) \cdot$ group in the cacotheline base, and that the resulting $\cdot CO \cdot$ group enters into complex union with the sulphite group; thus, (i) $\cdot CO \cdot CO \cdot + :CH \cdot OH \rightarrow \cdot C(OH) : C(OH) \cdot + :CO$, and (ii) $:NMe \cdot SO_3H + :CO \rightarrow :NMe \cdot SO_2 \cdot O \cdot C(OH) \cdot$. C. S.

Acid Esters of 2 : 6-Dimethylcinchomeronic Acid. RUD. WEGSCHEIDER (*Ber.*, 1918, **51**, 1478--1479).—Mumm and Hüneke's argument that the acid ester produced by the interaction of alcohol and the acid anhydride must be the γ -ester on steric grounds (*A.*, 1918, i, 183) is inadmissible, because the author has shown frequently (1895--1912) that in reactions of this kind the alcohol attacks the strongest carboxyl group present, even though it may be sterically protected. C. S.

New Cases of Isomerism in the Isatin Series. II. GUSTAV HELLER (*Ber.*, 1918, **51**, 1270--1281).—The existence of 5:7-dimethylisatin (and also of four dimethyl ethers) in four modifications (*A.*, 1918, i, 235) is now shown to be incorrect. 5:7-Dimethylisatin I is the lactam, $C_6H_2Me_2 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ NH \end{smallmatrix} CO$, since it exhibits all the reactions characteristic of isatin itself in the lactam form. The O-silver salt does not exist, the compound previously described as such being a complex substance containing very much more silver than the amount corresponding with the simple formula. The only silver derivative is the N-salt, and this reacts with methyl iodide in the presence of benzene at 100° to form the lactim ether, $C_6H_2Me_2 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ N \end{smallmatrix} C \cdot OMe$, m. p. 232° , which is identical with the previously described methyl ether of isomeride II (m. p. erroneously given as 247°). The sodium salt and methyl iodide yield the lactam ether.

Isomeride II.—This is produced from the isomeride I, has the same composition, is unimolecular, gives the indophenin reaction, and yields the preceding lactim ether by warming with methyl sulphate. It is therefore 5:7-dimethylisatin in the lactim form, which, unlike the corresponding form of isatin, is capable of isolated existence.

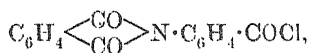
The lactim methyl ether is converted into 5:7-dimethylisatin (lactam) by boiling glacial acetic acid or hot dilute aqueous sodium hydroxide.

Since 5:7-dimethylisatin can exist in the lactam and the lactim forms, its salts may be N- or O-salts. The silver and the sodium salts prepared from the lactam regenerate this on acidification, and are thus N-salts, and therefore by analogy the silver and the sodium salts of isatin itself are lactam salts. No evidence of the formation of O-salts has been obtained.

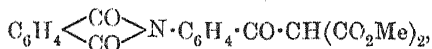
Isomeride III.—This is dimethylisatol, $C_6H_2Me_2 \llcorner \begin{smallmatrix} C(OH) \\ N \end{smallmatrix} \gg CO$. Its methyl ether is converted in the lactim ether by heating with 50% acetic acid.

Isomeride IV.—This substance, in the purest form obtained, crystallises in red needles, m. p. about 315° , sintering above 285° . It appears to contain a different ring system, and it is regenerated when its methyl ether is heated with 50% acetic acid. C. S.

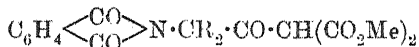
Action of Acylamino-acid Chlorides on Sodiomalonic Esters. V. S. GABRIEL and BRUNO LÖWENBERG (*Ber.*, 1918, 51, 1493-1500).—*o*-Phthaliminobenzoyl chloride,



stout prisms, m. p. 152 — 153° , prepared by heating *o*-phthaliminobenzoic acid with phosphorus pentachloride, reacts with a benzene suspension of methyl sodiomalonate to form the yellow sodium derivative of methyl *o*-phthaliminobenzoylmalonate,

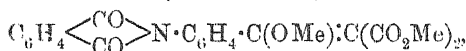


flat prisms, m. p. 159 — 161° . This substance, which is decomposed into methyl iodide, carbon dioxide, phthalic acid, and *o*-aminoacetophenone by boiling hydriodic acid, does not resemble the analogously constituted substances,



previously described by Gabriel (1913-1915) in its behaviour with sodium methoxide, since by treatment with a 4% methyl-alcoholic solution it yields, not the expected 6-ring analogue of the tetramic acids, but first the sodio-derivative, which then decomposes, yielding methyl *o*-phthaliminobenzoate, stout crystals, m. p. 160 — 162° (also prepared from *o*-phthaliminobenzoyl chloride and methyl-alcoholic sodium methoxide), and methyl 2-*o*-carboxybenzoylamino-

benzoate, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$, flat leaflets, m. p. 145—146° (also prepared by heating together methyl anthranilate and phthalic anhydride). A second point of difference is the behaviour of the sodio-derivative on methylation, since by heating with methyl iodide and acetone at 100°, it yields, not a C-methyl derivative, but the O-methyl derivative,



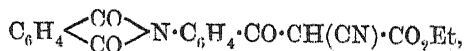
crystals, m. p. 148—149°, which is converted into phthalic and anthranilic acids by boiling hydrochloric or hydrobromic acid, but into methyl iodide, carbon dioxide, and a substance, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}$, flat needles or plates, m. p. 248° (decomp.), by hydriodic acid; this substance, which is probably 4-keto-2-o-carboxyphenyl-1:2:3:4-tetrahydroquinoline-3-carboxylic acid, yields carbon dioxide, aniline, and phthalidylacetic acid by heating at 180° with fuming hydrochloric acid.

Ethyl o-phthaliminobenzoylmalonate, $\text{C}_{22}\text{H}_{19}\text{O}_7\text{N}$, prisms, m. p. 101—107°, sintering at 94°, yields ethyl o-phthaliminobenzoate, stout prisms, m. p. 108—109°, and ethyl 2-o-carboxybenzoylamino-benzoate, needles, m. p. 114—116°, by treatment with sodium methoxide, and its sodio-derivative yields the O-ethyl derivative, $\text{C}_{24}\text{H}_{23}\text{O}_7\text{N}$, m. p. 89—90°, and O-methyl derivative, $\text{C}_{23}\text{H}_{21}\text{O}_7\text{N}$, prisms, m. p. 104—106°, from which the preceding dicarboxylic acid, $\text{C}_{17}\text{H}_{13}\text{O}_5\text{N}$, is obtained by the action of hydriodic acid.

C. S.

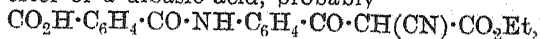
Some Quinoline Derivatives. S. GABRIEL (*Ber.*, 1918, 51, 1500—1515. Compare preceding abstract).—Since o-phthaliminobenzoylmalonic esters yield o-aminoacetophenone by treatment with acids (*loc. cit.*), o-phthaliminobenzoylcyanacetate esters have been prepared in the hope that they would yield o-amino- α -cyanoacetophenone, from which a quinoline derivative could be prepared. These expectations have been fulfilled.

Ethyl sodiocyanoacetate and o-phthaliminobenzoyl chloride react in benzene to form the yellow sodio-derivative of ethyl o-phthaliminobenzoylcyanacetate,



flat needles, m. p. 178—179°. The latter forms an ammonium derivative, yellow prisms, and a silver derivative, $\text{C}_{20}\text{H}_{13}\text{O}_5\text{N}_2\text{Ag}$, from which methyl iodide and acetone at 100° produce a methyl derivative, crystals, m. p. 173—174°, which is probably the O-ether, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{C}(\text{CN})\cdot\text{CO}_2\text{Et}$, since it yields the substance, $\text{C}_9\text{H}_8\text{ON}_2$, (see below) by boiling with hydriodic acid.

When treated with N-alkali hydroxide in the cold, and then with hydrochloric acid, ethyl o-phthaliminobenzoylcyanacetate yields the ester of a dibasic acid, probably



microscopic prisms or crusts, m. p. 263—265° (decomp.; sintering above 255°), which develops a cherry-red coloration with ferric chloride, and is converted by glacial acetic acid with warming into phthalic acid and 3-cyano-2:4-dihydroxyquinoline, $C_{16}H_8O_2N_2$, colourless needles, m. p. above 300° (decomp.; sintering at about 270°); the last substance is converted into 2:4-dihydroxyquinoline by boiling hydriodic acid, and into 2:4-dichloro-3-cyanoquinoline, colourless needles, m. p. 168—169°, by boiling with phosphoryl chloride and phosphorus pentachloride for one and a-half hours. If the boiling proceeds for only half an hour, the product is 4(or 2)-chloro-3-cyano-2(or 4)-hydroxyquinoline, flat needles, not molten at 280°. The dichlorocyanquinoline is converted into kynurenic acid by boiling hydriodic acid (b. p. 127°) and red phosphorus.

By boiling with hydrobromic or, better, hydriodic acid, ethyl *o*-phthaliminobenzoylcianoacetate is converted into phthalic acid and a substance, $C_9H_8ON_2$, long needles with $1H_2O$ from water or anhydrous crystals from alcohol, m. p. about 303—304°, sintering at about 285°, which forms a *hydrobromide*, $C_9H_8ON_2 \cdot HBr$, slender needles, *platinichloride*, and *aurichloride*, and is proved to be 2-amino-4-hydroxyquinoline, the intermediately formed *o*-amino-*o*-cyanoacetophenone not being isolated; a by-product of the reaction is 2:4-dihydroxyquinoline.

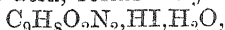
By treatment with nitric (D 1.30) and glacial acetic acids on the water-bath, 2:4-dihydroxyquinoline is converted into 3-nitro-2:4-dihydroxyquinoline, sulphur-yellow prisms, decomp. about 225°, which possesses pronounced acid properties and yields 2:4-dichloro-3-nitroquinoline, needles, m. p. 102°, by heating with phosphoryl chloride; the last substance is reduced to 3-aminoquinoline by tin and hydrochloric acid.

o-Nitrobenzoyl chloride reacts with ethyl sodiocyanoacetate in the presence of ether to form, after treatment of the initial product with hydrochloric acid, ethyl *o*-nitrobenzoylcianoacetate, $NO_2 \cdot C_6H_4 \cdot CO \cdot CH(CN) \cdot CO_2Et$, needles, m. p. 91°, which is reduced and hydrolysed by boiling hydriodic acid and red phosphorus, yielding ethyl iodide, carbon dioxide, and 2-amino-4-hydroxyquinoline. The aminohydroxyquinoline is converted by very dilute hydrochloric acid and alkali nitrite (1 mol.) into the *iminoquinisatoxime*, $C_6H_4 \begin{smallmatrix} NH \cdot C \cdot NH \\ \diagdown \quad \diagup \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$ or $C_6H_4 \begin{smallmatrix} N = C \cdot NH_2 \\ \diagdown \quad \diagup \\ CO \cdot C \cdot N \cdot OH \end{smallmatrix}$, which forms

a *potassium salt*, $C_6H_4O_2N_3K$, garnet-red needles, and a *hydrochloride*, $C_6H_7O_2N_3 \cdot HCl$, orange-yellow needles, yields 3-nitro-2:4-dihydroxyquinoline by warming with nitric acid (D 1.34), and is reduced by tin and 20% hydrochloric acid to the *hydrochloride*, colourless crystals containing $1H_2O$, of a *base*, $C_6H_8O_2N_2$, needles containing $1H_2O$, not molten at 300°, which is probably 2-amino-3:4-dihydroxyquinoline. By trituration with hydriodic acid (b. p. 127°), the iminoquinisatoxime is converted into 2:3-diamino-4-hydroxyquinoline, flat needles (*hydrochloride*, $C_6H_9ON_3 \cdot 2HCl$, needles).

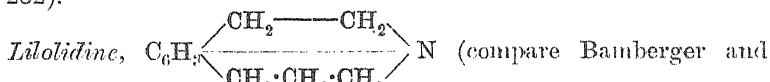
The reduction of quinisatoxime by hydriodic acid or by tin and

20% hydrochloric acid yields the *hydrochloride*, $C_9H_8O_2N_2 \cdot HCl \cdot H_2O$, colourless needles, not molten at 285° , of 3-*amino*-2:4-*dihydroxyquinoline*, microscopic needles, not molten at 280° . The base, which is also obtained by reducing 3-nitro-2:4-dihydroxyquinoline by tin and hydrochloric acid, forms a *hydriodide*,



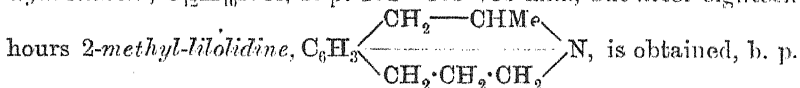
colourless needles, and an *acetyl* derivative, darkening above 200° , but not molten at 285° . C. S.

Bases of the Julolidine Type. J. VON BRAUN, KARL HEIDER, and WANDA WYCZATKOWSKA (*Ber.*, 1918, 51, 1215—1227).—Such bases are of interest in connexion with the phenomena of steric hindrance in tertiary bases and the fission of hydrogenised indole and quinoline derivatives by sodium amalgam (von Braun, A., 1917, i, 282).



Sternitzki, A., 1893, i, 520), b. p. $156^\circ/15$ mm., cannot be prepared from tetrahydroquinoline and ethylene dibromide, but is produced by gently boiling a mixture of dihydroindole (1 part) and γ -chloropropyl bromide (6 parts) for eighteen hours. It forms a *picrate*, m. p. 138° , and a *methiodide*, and resembles dimethylaniline in its behaviour towards formaldehyde, yielding a viscous diphenylmethane derivative, $CH_2(C_{11}H_{12}N)_2$, and towards benzaldehyde in the presence of zinc chloride, yielding ultimately an intensely green substance. The *methochloride* exhibits remarkable stability towards 5% sodium amalgam, the rings being unbroken and lilolidine being regenerated. This stability is in marked contrast to those of the methochlorides of tetrahydroquinoline and dihydroindole, in which the rings are ruptured to the extent of 60% and 25% respectively.

2-Methyldihydroindole and γ -chloropropyl bromide, boiled together for four to five hours, yield 2-methyl-1- γ -chloropropyl-dihydroindole, $C_{12}H_{16}NCl$, b. p. $172\text{---}175^\circ/15$ mm., but after eighteen



$165\text{---}167^\circ/15$ mm., which forms a *picrate*, m. p. 140° , and a *methiodide*, m. p. 202° , resembles lilolidine in its behaviour towards formaldehyde and benzaldehyde, and the *methochloride* of which is mainly unruptured by sodium amalgam, only about 10% of it being converted into a *base*, $C_{13}H_{19}N$, colourless oil, b. p. $151^\circ/15$ mm. (*picrate*, yellow needles, m. p. 121° ; *platinichloride*, m. p. $177\text{---}178^\circ$). This base, which yields a *m*-diamine by nitration and subsequent reduction, must be 1:2-dimethyl-1-*n*-propyldihydroindole, because it is not identical with the only other substance possible, namely, 8-*n*-propylkairolone. The last-mentioned substance was synthesised as follows: *o*-Propylaniline, obtained from tetrahydroquinoline through *o*- γ -chloropropylbenzanilide, is converted by

the Skraup method into 8-propylquinoline, b. p. 142°/15 mm. (platinichloride, m. p. 196°; picrate, yellowish-red needles, m. p. 142°), the methiodide, m. p. 136°, of which is reduced by tin and hydrochloric acid to 8-n-propylkairoline (picrate, m. p. 108—109°; platinichloride, m. p. 164°).

Julolidine, prepared by Pinkus's method (A., 1892, 1491. For large quantities of materials the time of heating must be prolonged to eight hours to prevent the formation of halogenated impurities), resembles the lilolidines in its behaviour towards benzaldehyde and formaldehyde (the oily diphenylmethane derivative yields a dimethiodide, $C_{27}H_{36}N_2I_2$, colourless crystals, m. p. 228°, and forms a methiodide much more readily than does 8-methylkairoline or dimethyl-o-toluidine. The methochloride by reduction with 5% sodium amalgam yields 63% of julolidine and 37% of a base, $C_{13}H_{19}N$, b. p. 144—148°/23 mm. (picrate, yellow needles, m. p. 189°, decomposition beginning above 180°; platinichloride, m. p. 191°; methiodide, colourless crystals, m. p. 200°), which is not the expected 8-n-propylkairoline, but appears to have the annexed formula. It is remarkable in that it contains a 10-ring, and is a meta-bicyclic compound. It is a saturated substance, yields isophthalic acid by oxidation with alkaline permanganate, does not condense with benzaldehyde to give ultimately a green colouring matter, does not yield a meta-diamine by nitration and subsequent reduction, and its methiodide, after treatment with silver oxide and distillation, yields a base, $C_{14}H_{21}N$, b. p. 117—118°/3 mm., which does not form crystalline salts, is unsaturated and is regarded as γ -3-allylphenyl-n-propyldimethylamine, $CH_3:CH:CH_2 \cdot C_6H_4 \cdot [CH_2]_3 \cdot NMe_2$.

C. S.

Proteinogenous Amines. I. Synthesis of β -Iminazolyethylamine [Histamine]. KARL K. KOESSLER and MILTON TH. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 1716—1726).—The method followed is based on that of Pyman (T., 1911, **99**, 668), but several additions and improvements have been effected. Full descriptions are given of the preparation of acetonedicarboxylic acid, dioximinoacetone, diaminoacetone stannichloride, diaminoacetone hydrochloride, 2-thiol-4(or 5)-aminomethylglyoxaline hydrochloride, 4(or 5)-hydroxymethylglyoxaline picrate, 4(or 5)-hydroxymethylglyoxaline hydrochloride, and of iminazolyethylamine dichloride (histamine dichloride); the separation of methylglyoxaline and of glyoxalineacetic acid is also described. One hundred and sixty-five grams of histamine dichloride are obtained from 4530 grams of citric acid.

H. W.

Phenomena of Luminescence in Pyrazoline Derivatives. FRITZ STRAUS [with CARL MUFFAT and W. HEITZ] (*Ber.*, 1918, **51**, 1457—1477).—In consequence of the striking ease with which pyrazolines are obtained directly by the action of phenylhydrazine

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on phenyl styryl ketone, distyryl ketone, and ethyl γ -keto- $\Delta^{\alpha\epsilon}$ -pentadiene- $\alpha\epsilon$ -dicarboxylate, the intermediary phenylhydrazones not being isolable, and of the phenomena of luminescence exhibited by these substances, the reaction has been extended to include a series of substituted ketones and substituted hydrazines. It is found that pyrazolines are formed except (1) when *p*-nitrophenylhydrazine is used, (2) when an *o*-methoxy-group is present in the phenyl group of the ketone, and (3) when the phenylhydrazine and a phenyl group of the ketone both contain a halogen substituent; in these three cases the phenylhydrazones or substituted phenylhydrazones are stable, and require special treatment for their conversion into pyrazolines.

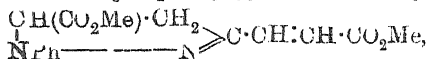
The following substances are described. The method of von Auwers and Voss (A., 1910, i, 70), reduction by sodium amalgam with the formation of aniline, is used to distinguish the phenylhydrazones from the pyrazolines.

1- α -Naphthyl-5-phenyl-3-styrylpyrazoline, prepared from distyryl ketone and α -naphthylhydrazine in boiling alcohol, forms yellow needles with green fluorescence, m. p. 164°; the β -naphthyl isomeride, m. p. 195°, has a similar appearance. 5-Phenyl-1-*p*-bromophenyl-3-styrylpyrazoline, prepared in glacial acetic acid solution at the ordinary temperature, forms yellow needles with green fluorescence, m. p. 177°. Distyryl ketone *p*-nitrophenylhydrazone, yellowish-red leaflets, m. p. 173°, yields *p*-phenylenediamine by reduction with sodium amalgam, and is converted into 5-phenyl-1-*p*-nitrophenyl-3-styrylpyrazoline, yellowish-red crystals with intense green fluorescence, m. p. 204—205°, by boiling glacial acetic acid. Di-*o*-methoxystyryl ketone phenylhydrazone, brownish-yellow crystals, m. p. 142°, is converted into 1-phenyl-5-*o*-methoxyphenyl-3-*o*-methoxystyrylpyrazoline, pale yellow crystals with greenish-blue fluorescence, m. p. 153—154.5°, in a similar manner. 1-Phenyl-5-*p*-methoxyphenyl-3-*p*-methoxystyrylpyrazoline, prepared in boiling benzene, or, more simply, hot glacial acetic acid solution, forms pale yellow leaflets, m. p. 159°, which are so intensely fluorescent that they appear almost green. 1-Phenyl-5-*p*-dimethylaminophenyl-3-*p*-dimethylaminostyrylpyrazoline forms yellow needles, m. p. 192°, which exhibit an extraordinarily intense green fluorescence.

Di-*o*-chlorostyryl ketone, yellow needles, m. p. 125°, prepared from *o*-chlorobenzaldehyde and acetone in 5% boiling alcoholic sodium methoxide solution, reacts with *p*-bromophenylhydrazine by prolonged keeping in glacial acetic acid in the cold to form the *p*-bromophenylhydrazone, $C_{23}H_{17}N_2Cl_2Br$, dark yellow crystals, m. p. 145°, but yields by treatment with phenylhydrazine in boiling alcohol containing a little acetic acid 1-phenyl-5-*o*-chlorophenyl-3-*o*-chlorostyrylpyrazoline, yellow needles, m. p. 145°, forming a green, fluorescent solution in alcohol. 1-Phenyl-5-*p*-chlorophenyl-3-*p*-chlorostyrylpyrazoline, m. p. 212°, forms yellow needles with intense green fluorescence; its solution in concentrated sulphuric acid is so slightly coloured by ferric chloride that some doubt would exist as to the substance being a pyrazoline were it not that aniline is not

produced by its reduction by sodium amalgam. *Di-p-chlorostyryl ketone p-bromophenylhydrazone*, yellow needles, m. p. 183°, which become brown in air, yields *p*-bromoaniline by reduction with sodium amalgam, and is converted into 5-*p-chlorophenyl*-1-*p-bromophenyl*-3-*p-chlorostyryl*pyrazoline, yellow needles with intense green fluorescence, m. p. 173—174°, by boiling glacial acetic acid.

Methyl 5-carbomethoxy-1-phenylpyrazoline-3-acrylate,



m. p. 153°, yellow leaflets with a striking green fluorescence, is prepared from phenylhydrazine and methyl γ -keto- Δ^5 -pentadiene- α -dicarboxylate (Straus, A., 1904, i, 851) in boiling benzene. The *ethyl ester*, $\text{C}_{17}\text{H}_{20}\text{O}_4\text{N}_2$, yellow, fluorescent leaflets, m. p. 92.5°, yields the *acid*, $\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2$, yellow needles, m. p. 204° (decomp.), by hydrolysis with aqueous-alcoholic sodium hydroxide on the water-bath. The preceding methyl ketopentadienedicarboxylate forms a *phenylmethylhydrazone*, $\text{C}_{16}\text{H}_{18}\text{O}_4\text{N}_2$, dark red crystals, m. p. 105°, and the ethyl ester forms a *p-bromophenylhydrazone*, $\text{C}_{17}\text{H}_{19}\text{O}_4\text{N}_2\text{Br}$, reddish-yellow needles, m. p. 134°.

When boiled with glacial acetic acid, the phenylhydrazones of phenyl cinnamylidenemethyl ketone and of dicinnamylidenemethyl ketone are converted respectively into substances, $\text{C}_{23}\text{H}_{20}\text{N}_2$, colourless crystals with faint blue fluorescence, m. p. 123—124°, and $\text{C}_{27}\text{H}_{24}\text{N}_2$, orange-yellow needles, m. p. 142°, which are not pyrazolines because they cannot be oxidised to the pyrazolinecarboxylic acids.

Straus and Ackermann's *p*-chlorophenyl *p*-chlorostyryl ketone phenylhydrazone (A., 1909, i, 489) is really 1-phenyl-3:5-di-*p*-chlorophenylpyrazoline, and Minnuni's distyryl ketone phenylhydrazone (A., 1900, i, 237) is 1:5-diphenyl-3-styrylpyrazoline.

All the pyrazolines examined exhibited the most intense fluorescence when exposed to Röntgen rays. An apparatus is described by which several substances can be simultaneously but separately exposed to the rays with or without passage through zinc foil, and the intensities of the fluorescence compared with that of barium platincyanoide. The fluorescence is still visible after the rays have passed through zinc foil 0.6 mm. in thickness. A new noteworthy fact is that the fluorescence is observed, not only with the crystalline substances, but also with their solutions, the intensity being greatly influenced by the nature of the solvent. In the case of a 1% solution of the ester of 5-carboxy-1-phenylpyrazoline-3-acrylic acid, the solutions in alcohol and glacial acetic acid were only feebly fluorescent, and the fluorescence was destroyed by interposing zinc foil 0.2 mm. thick, but the solutions in carbon disulphide, benzene, and chloroform were intensely fluorescent, and a thickness of 1 mm. of zinc foil was necessary to destroy it.

There is a noteworthy difference between the fluorescence of the 1:3:5-trisubstituted pyrazolines excited by Röntgen rays and that produced by diffuse daylight. The excitation of Röntgen rays occurs

within narrow limits, and is connected with the presence of an unsaturated group (phenyl or carbonyl) in positions 3 and 5; if these positions are occupied by hydrogen or by an aliphatic group the pyrazoline fluoresces in diffuse daylight, but is unaffected by Röntgen rays. The effects on the intensity of the fluorescence of substituents in phenyl groups in positions 1, 3, and 5 are discussed. The phenylhydrazones of unsaturated ketones are intensely coloured, but do not exhibit a trace of fluorescence. C. S.

Preparation of Mercurous Amino-compounds. SCHWEIZ. SERUM- & IMPFINSTITUT (D.R.-P., 307893; from *Chem. Zentr.*, 1918, ii, 693).—The compounds are prepared by the action of one or more molecules of a mercurous salt on 1-phenyl-2:3-dimethyl-5-pyrazolone-4-sulphonamide. The substance obtained with mercurous sulphate (1 mol.) is a greyish-white, crystalline mass, which darkens and swells when heated; it is specifically lighter than mercurous sulphate, and contains 40% of mercury. On treatment with alkali it yields a precipitate of mercury and a soluble mercuric amino-compound, which is precipitated by hydrogen sulphide after acidification with hydrochloric acid. With two molecules of mercurous sulphate a complex substance is formed. The compounds are stable in substance and also when emulsified with fats. They have marked bactericidal and spirillicidal properties. H. W.

Salts of Helianthin. CHARLES R. STARK and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1918, **40**, 1573—1580).—Recent studies with methyl-orange (Dehn, A., 1917, i, 594) have led to the conclusion that colour changes in solution are largely or wholly independent of ionic concentrations. It has been suggested that the coloured solute forms additive compounds with acids, bases, or indifferent solvents. In the present communication it is shown that helianthin forms salts with great ease, all of which can be interpreted as additive compounds.

The helianthin salts of bases were prepared (1) from aqueous solutions of helianthin and the free base, (2) by double decomposition from methyl-orange and the salt of the base, (3) by adding helianthin to the pure liquid base, and (4) by treating helianthin with an excess of the base dissolved in absolute ether. In the preparation of helianthin salts with acids, the presence of water must be avoided; the salt is conveniently obtained by dissolving helianthin in excess of the warm acidic solvent and subsequently adding ether.

Salts of helianthin prepared in aqueous solution with inorganic bases always contain two molecules of water to each helianthin residue. The salts made with ammonia or volatile organic bases give free helianthin when heated; those containing the coloured ions Cr'' , Cu'' , Co'' , Ni'' , Fe'' or Fe''' give no evidence of the presence of these ions if they are judged only by the colour; when dehydrated, all helianthin salts containing the bivalent and trivalent metals, but not the univalent metals, tend to form the colour of helianthin itself. The salts of organic bases are always additive compounds of the type $\text{C}_{14}\text{H}_{14}\text{N}_3\text{SO}_3\text{H}$ base. The salts with the

following metals or bases are described: *Aluminium*, golden, rhombic plates; *ammonium*, m. p. 225°, large golden-red, rhombic plates; *barium*, golden-brown, rhombic plates; *cadmium*, golden-red rhombic plates; *calcium*, orange needles and rhombic plates; *chromium*, golden-brown, rhombic plates; *cobalt*, golden-red, hexagonal and rhombic plates; *copper*, pale golden-brown, rhombic plates; *ferrous*, m. p. 209°, golden-brown, rhombic plates; *ferrie*, reddish-golden, irregular and rhombic plates; *lead*, brown masses and irregular plates; *magnesium*, reddish-gold, hexagonal and rhombic plates; *manganese*, pale reddish-gold, irregular and rhombic plates; *silver*, dull brownish-red needles; *sodium*, m. p. 224°; *nickel*, light golden-red, hexagonal and rhombic plates; *potassium*, orange, hexagonal plates, m. p. 300°; *strontium*, brilliant orange, rhombic plates and needles; *uranium*, orange-red, rhombic plates; *zinc*, golden-brown, rhombic plates, m. p. 241°; *aniline*, golden-orange, prismatic flakes and needles, m. p. 211°; *benzidine*, golden-brown, irregular and rectangular plates and needles, m. p. 198° after changing at 194°; *brucine*, orange, prismatic needles, m. p. 224°; *cinchonidine*, light yellow, prismatic needles and irregular plates, m. p. 155°, after changing at 146°; *dimethylaniline*, needles and hexagonal plates; *methylaniline*, thin, golden-brown prisms and rhombic and hexagonal plates, m. p. 167°; *morphine*, bright orange, irregular plates and sheaves and wart-like masses of prisms, m. p. 219°; *α-naphthylamine*, dull brown needles, m. p. 211°; *β-naphthylamine*, brownish-yellow, thin, irregular plates, m. p. 209°; *phenylhydrazine*, orange needles and rectangular plates, m. p. 165°; *α-picoline*, dark brownish-red, rectangular and octagonal plates, m. p. 180°, after changing at 157°; *piperidine*, bright orange, octagonal and irregular plates, m. p. 223°; *quinine*, orange, amorphous mass, m. p. 158°; *quinoline*, orange-red prisms and octagonal plates, m. p. 194°; *strychnine*, golden-orange prisms and rectangular and irregular plates, m. p. 254°; *o-toluidine*, orange-red, prismatic needles, m. p. 203°; *m-toluidine*, golden-yellow needles and irregular plates, m. p. 202°.

Helianthin phenolate forms dark purple prisms, m. p. 200°.

The solubilities of the salts in water and their behaviour when heated are recorded in a series of tables, for which the original must be consulted. H. W.

Synthesis of some New Substantive Dyes derived from Benzidine-Sulphone. HUGH RYAN, JOSEPH ALGAR, and PHILIP O'CONNELL (*Proc. Roy. Irish Acad.*, 1918, **34**, (B), 85—96).—A series of dyes of the benzidine type has been prepared by coupling hydroxy- and amino-compounds with the tetrazo-derivative of benzidine-sulphone-disulphonic acid. The dyes have been isolated in the form of pure sodium salts; they act as direct dyes towards cotton and the colours are unaffected by washing. *Products* have been obtained with the following substances, the shade obtained on cotton being placed within brackets: naphthionic acid, dull blue, amorphous powder (purple); *β*-naphthylamine, red, amorphous

powder (violet-red); α -naphthylamine, dark red powder (navy blue); salicylic acid, reddish-brown powder (orange); "R" acid, reddish-blue powder (violet-red); "S" acid, red, amorphous powder (pink); "H" acid, dark blue powder (light blue); β -naphthol-6-monosulphonic acid, dark blue, amorphous powder (light purple); catechol, dark blue powder (light brown); resorcinol, dark blue powder (maroon); quinol, brown powder (buff); pyrogallol, chocolate-brown powder (buff); gallic acid, dark brown powder (light brown); sulph-anilic acid, orange-red, amorphous powder (canary-yellow); dimethylaniline, dark blue powder (deep purple). H. W.

Influence of Substituents on Reactions. II. Rate of Reduction of Polymethylphenylhydrazines. HARTWIG FRANZEN, ARVID ONSAGER, and GUNNAR FAERDEN (*J. pr. Chem.*, 1918, [ii], 97, 336—352. Compare A., 1918, i, 456).—Continuing the previous investigation, the authors have examined the rate of reduction by stannous chloride and hydrochloric acid of phenylhydrazines containing several nuclear methyl substituents. In the case of the dimethylphenylhydrazines the series, arranged in order of decreasing ease of fission, is precisely that which would be predicted from the previous results, the values of the constant K' being: 2:6-dimethylphenylhydrazine, 4.19; 2:4-, 2.49; 2:3-, 0.130; 2:5-, 0.107; 3:4-, 0.102. The 3:5-compound has been only provisionally examined, and its rate of reduction appears to be less than that of the 3:4-compound.

The only trimethylphenylhydrazines that have been examined are the 2:4:6- and 2:4:5-compounds. The entrance of yet another methyl group still further increases the ease of fission by stannous chloride and hydrochloric acid. These two compounds are reduced so rapidly at 100° that measurements cannot be made. At 80° the K' value of the former is 3.99 and of the latter 1.05. These values will be about six times as great at 100°, so that at this temperature 2:4:6-trimethylphenylhydrazine is reduced about six times more rapidly than 2:6-dimethylphenylhydrazine and about 1200 times more rapidly than phenylhydrazine itself.

The striking parallelism traced between the rate of reduction of substituted phenylhydrazines and the rate of dehalogenation of correspondingly substituted halogenobenzenes by hydriodic acid (*loc. cit.*) is still more evident in the case of the dimethylphenylhydrazines and the iododimethylbenzenes. After boiling with hydriodic acid for five hours the amounts of xylene obtained are: from 2-iodo-1:3-dimethylbenzene, 80%; from 4:1:3-, 60%; from 3:1:2-, trace; from 2:1:4-, trace; from 1:3:5-, 0%. 2-Iodo-1:3:5-trimethylbenzene yields 50% of mesitylene after boiling for five hours and 90% after being heated at 140° for five hours, the corresponding values for 5-iodo-1:2:4-trimethylbenzene being 0% and 85% of ψ -cumene respectively.

The polymethylphenylhydrazines required in the investigation were prepared by reducing the diazonium chlorides with stannous chloride and hydrochloric acid. In several cases the yields were

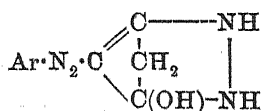
very bad, as low as 7.5%, in consequence of the reaction $\text{ArN}_2\text{Cl} + 2\text{H} = \text{ArH} + \text{N}_2 + \text{HCl}$ becoming the main reaction. A relation was found to exist between the rate of reduction of the polymethylphenylhydrazines and the tendency of the corresponding diazonium chlorides to yield the phenylhydrazine or the hydrocarbon and nitrogen on reduction; the more easily the phenylhydrazine is reduced the greater is the tendency of the corresponding diazonium chloride to yield the hydrocarbon and nitrogen on reduction.

3-*o*-Xylylhydrazine, colourless needles, m. p. 108°, forms a *hydrochloride*, colourless leaflets, m. p. 208°, *benzylidene* derivative, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{CHPh}$, yellow crystals, m. p. 68°, *p*-anisylidene derivative, dark yellow, crystalline powder, m. p. 98°, and *dibenzoyl* derivative, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NBz} \cdot \text{NHBz}$, colourless, crystalline powder, m. p. 198°. *Pyruvic acid* 3-*o*-xylylhydrazone, $\text{CO}_2\text{H} \cdot \text{CMe} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Me}_2$, forms yellow leaflets, m. p. 166°.

2:4:6-Trimethylphenylhydrazine hydrochloride forms faintly yellow leaflets. C. S.

Synthesis of New Chloroarylhydrazones of Oxalomono-ester and -mono-amide Acid Chlorides and of the Corresponding Nitriles. CARL BÜLOW and RICHARD ENGLER (*Ber.*, 1918, 51, 1246—1270).—In consequence of its decomposition by heat into carbon monoxide and ethyl malonate, ethyl oxalacetate is represented by the "aliphatic cyclic" structure, $\text{CO} < \begin{matrix} \text{CH} \cdot \text{CO}_2\text{Et} \\ \text{C}(\text{OH}) \cdot \text{OEt} \end{matrix}$ (compare Bülow and Huss, A., 1918, i, 314); citric acid, ethyl acetonedicarboxylate, ethyl formylacetate, ethyl acetoacetate, and acetylacetone are represented by similar 3-ring and 4-ring structures containing the group $\cdot\text{CH}:\text{C}(\text{OH})\cdot$ similar to that in β -naphthol, and therefore reacting with diazonium salts. Ethyl *o*-tolueneazoacetoacetate, for example, is represented by the formula $\text{C}(\text{OH}):\text{C} \cdot \text{N}_2 \cdot \text{C}_6\text{H}_7$
 $\text{CH}_2 - \text{C}(\text{OH}) \cdot \text{OEt}$. This substance, previously prepared by Bülow

and Schaub (A., 1908, i, 704), has m. p. 52° (Bülow and Schaub give 67°), yields the corresponding *potassium* salt, yellow needles, by hydrolysis with boiling 1% potassium hydroxide, and by treatment with concentrated nitric acid and subsequently with water is converted into nitrated *o*-toluenediazonium nitrate and ethyl acetoacetate. When treated with concentrated nitric acid in cold glacial acetic acid solution, however, it yields *ethyl nitro-o-tolueneazoacetoacetate*, needles, m. p. 135—136°, since the product and hydrazine hydrate in hot glacial acetic acid yield 4-*nitro-o-tolueneazo-3-methylpyrazolone*, yellowish-orange needles, m. p. 223—224° (decomp.). To azopyrazolones the authors give the formula (annexed). By chlorination in cold alcoholic solution and repetition of the treatment on the initial product in warm alcohol, ethyl *o*-tolueneazoacetoacetate yields *ethyl α -chloroglyoxylate*



5-chloro-*o*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : CCl \cdot CO_2Et$, colourless needles, m. p. 110° , which yields 5-chloro-*o*-toluidine by reduction with hydrochloric acid and zinc dust, and is converted by potassium cyanide in aqueous-alcoholic solution into ethyl α -cyanoglyoxylate 5-chloro-*o*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : C(CN) \cdot CO_2Et$, golden-yellow needles, m. p. 163.5° , identical with the substance prepared by condensing diazotised 5-chloro-*o*-toluidine and ethyl cyanoacetate. The product obtained by the latter method is a labile form, which changes at its m. p., 106.5° , into the stable form, m. p. 163.5° . Ethyl α -chloroglyoxylate 5-chloro-*o*-tolylhydrazone resembles ethyl *o*-tolueneazoacetate in its behaviour with concentrated nitric acid and exhibits halochromy when dissolved in concentrated sulphuric acid, the solution developing an intense yellow colour, which changes very rapidly to a dirty brownish-green, and regenerating the original substance on the addition of water. Ethyl α -cyanoglyoxylate 5-chloro-*o*-tolylhydrazone, by treatment with concentrated nitric acid at about $40-50^\circ$ and subsequently with water, yields a nitrated product, m. p. $121-122^\circ$, together with a comparatively large amount of a diazonium nitrate.

By treatment with 96% alcohol and aqueous ammonia, ethyl *o*-tolueneazoacetate yields, in addition to a small amount of the ammonium salt, m. p. 202° (decomp.), *o*-tolueneazoacetamide, golden-yellow needles, m. p. 142° , which yields nitro-*o*-tolueneazoacetamide, m. p. $243-244^\circ$, and only a trace of a diazonium salt by treatment with concentrated nitric acid at about 45° . The preceding ammonium salt yields *o*-tolueneazoacetic acid, greenish-yellow needles, m. p. $137-138^\circ$, by treatment with glacial acetic acid.

Ethyl *p*-tolueneazoacetate is very readily converted into the corresponding potassium salt by boiling 1-2% potassium hydroxide and resembles the ortho-isomeride in its behaviour towards concentrated nitric acid, yielding partly a diazonium salt by fission and partly ethyl nitro-*p*-tolueneazoacetate, m. p. $143-144^\circ$, which is converted into 4-nitro-*p*-tolueneazo-3-methylpyrazolone, m. p. 234° , by hydrazine hydrate in glacial acetic acid solution.

Ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone, m. p. 100° , is prepared like the preceding *o*-tolyl isomeride, but when chlorinated in carbon tetrachloride at 0° ethyl *p*-tolueneazoacetate yields ethyl α -chloroglyoxylate *p*-tolylhydrazone, colourless needles, m. p. $101-101.5^\circ$. Both these hydrazones yield diazonium salts by treatment with nitric acid. The former reacts with potassium cyanide to form ethyl α -cyanoglyoxylate 3-chloro-*p*-tolylhydrazone, golden-yellow needles, m. p. 160° , which undergoes both nitration and fission by treatment with nitric acid, and in cold alcoholic suspension reacts with chlorine in a unique manner, yielding 3-chloro-*p*-toluenediazonium chloride, ammonium chloride, and the decomposition products of ethyl hydrogen dichloromalonate. Ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone yields 3-chloro-*p*-toluidine by reduction with hydrochloric acid and zinc dust. Ethyl α -cyanoglyoxylate 3-chloro-*p*-tolylhydrazone has also been prepared

by condensing diazotised 3-chloro-*p*-toluidine with ethyl cyanoacetate.

p-Tolueneazoacetoacetamide, prepared by treating an alcoholic solution of ethyl *p*-tolueneazoacetoacetate with a large excess of concentrated aqueous ammonia, forms pale green leaflets, m. p. 173°, yields nitro-*p*-tolueneazoacetoacetamide, m. p. 211—212°, and a little diazonium salt by treatment with concentrated nitric acid, and yields by chlorination in boiling alcoholic solution α -chloroglyoxylamide 3-chloro-*p*-tolylhydrazone, $C_6H_3MeCl \cdot NH \cdot N : CCl \cdot CO \cdot NH_2$, colourless needles; the constitution $C_6H_3MeCl \cdot NH \begin{smallmatrix} NH=CCl \\ \backslash \\ NH-CO \end{smallmatrix}$ is suggested to account for the absence of colour. C. S.

Preparation of Bromolecithalbumin and Bromolecithin. PETER BERGELL (D.R.-P., 307490; from *Chem. Zentr.*, 1918, ii, 494—495).—Lecithalbumin is treated with bromine in anhydrous, indifferent organic solvents, and, when required, the bromolecithalbumin is decomposed into bromolecithin and albumin according to the method of converting lecithalbumin into lecithin. *Bromolecithalbumin* is a pale yellow, almost odourless powder with a faintly acid taste and reaction; it contains about 16.6% of bromine. It is transformed by methyl or ethyl alcohol, slowly in the cold more rapidly on warming, into albumin and *bromolecithin* containing up to 25% of bromine. H. W.

The Relationship between Diastase, Peroxydase, and Catalase. H. MAGGI (*Helv. Chim. Acta*, 1918, 1, 433—451).—The simultaneous presence of peroxydase and catalase activity in many ferments has been attributed by Woker (A., 1917, i, 447) to the presence of an aldehydic group which unites with hydrogen peroxide to yield a secondary peroxide, $OH \cdot CHR \cdot O \cdot OH$, which has more powerful oxidising properties than hydrogen peroxide itself and also reacts with an excess of the latter to yield oxygen. The author has examined the question of the possibility of the aldehyde group being able to exert diastatic action, in addition to peroxydising and catalytic action, and suggests that the mechanism would consist in the alternate addition (to form a hydrate) and elimination of water.

The action of mixtures of starch and formaldehyde has been investigated by the capillarity method; the presence of dextrans is detected by means of iodine and of sugars by Fehling's solution. The results show that the behaviour of formaldehyde towards starch closely resembles that of diastase. One considerable difference, the recurrence of the blue coloration with lapse of time in the case of mixtures of formaldehyde and starch, has been further investigated. The phenomenon appears to be due to the formation of unstable iodine derivatives of formaldehyde or of the achroodextrans which gradually eliminate iodine. The following conditions are necessary: (i) unchanged starch, and (ii) a substance capable of liberating iodine, must be present; if these conditions are fulfilled, any

elimination of achroodextrins by combination, fission, or by any other method can restore the blue colour to the solution. H. W.

Nitro- and Amino-arylsarsinic Acids. WALTER A. JACOBS, MICHAEL HEIDELBERGER and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1918, **40**, 1580—1590).—The preparation of a number of nitro- and amino-arylsarsinic acids is described; the nitro-compounds are generally obtained by Bart's method (D.R.-P., 250264), in which a diazo- or isodiazo-group is replaced by the arsinic acid residue. This procedure is particularly serviceable with *o*- and *p*-nitroamines; with *m*-nitroamines, on the other hand, the yields are poor, though better with *m*-nitrotoluidines than with *m*-nitroaniline. Reduction of the nitro- to the amino-group without disturbance of the arsinic acid residue is conveniently effected with cold, alkaline ferrous hydroxide solution (compare Benda, A., 1912, i, 63). The following compounds have been prepared by these methods:—*o*-nitrophenylarsinic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$, m. p. 235—240° (decomp.) [compare Bart, *loc. cit.*]; *o*-aminophenylarsinic acid (compare Benda, *loc. cit.*), needles, m. p. 153°; *m*-aminophenylarsinic acid (compare Berthelm, A., 1908, i, 590; Berthelm and Benda, A., 1912, i, 62), colourless, rhombic prisms, m. p. 213—215° (decomp.); *p*-nitrophenylarsinic acid (compare Bart, *loc. cit.*), pale yellow aggregates of minute leaflets, which do not melt below 275°; *p*-aminophenylarsinic acid; 2-nitro-*p*-tolylarsinic acid, faintly yellow, minute rods, m. p. 255—260° (decomp.); 2-amino-*p*-tolylarsinic acid, colourless needles, m. p. 180°, after softening and darkening; 6-nitro-*o*-tolylarsinic acid, pale yellow needles decomposing at 228—230°; 6-amino-*o*-tolylarsinic acid, rosettes or plates decomposing at 175—180°; 5-nitro-*p*-tolylarsinic acid (compare Michaelis, A., 1902, i, 411), cream-coloured needles which do not melt below 285°; 5-amino-*p*-tolylarsinic acid, microscopic needles, m. p. 172—175°; 5-nitro-*o*-tolylarsinic acid (compare Karrer, A., 1915, i, 333), m. p. 261—263° (decomp.), after melting or changing in appearance at about 225° according to the rate of heating; 5-amino-*o*-tolylarsinic acid, cream-coloured prisms decomposing at 235—245°; 4-nitro-*o*-tolylarsinic acid, minute needles, m. p. 235—240° (decomp.); 4-amino-*o*-tolylarsinic acid, microscopic needles, decomposing at 222—224° (Benda and Kahn, A., 1908, i, 591, give 180°); 4-nitro-*p*-xylylsarsinic acid, yellow crystals, m. p. 290° (decomp.), which is not identical with the substance obtained by Michaelis (*loc. cit.*) by the nitration of *p*-xylylsarsinic acid; 4-amino-*p*-xylylsarsinic acid (compare Benda and Kahn, *loc. cit.*), colourless platelets, m. p. 213—214° (decomp.); 3-amino-4-hydroxyphenylarsinic acid, decomposing at 290° after darkening and softening at about 220°. H. W.

Silicon-Hydrocarbons with Nuclei containing Halogens, and their Use in Syntheses. GERHARD GRÜTTNER and MARIANNE CAUER (*Ber.*, 1918, **51**, 1283—1292. Compare Grüttner and Krause, A., 1918, i, 132).—An extension of the earlier work. Trichloro-*p*-bromophenylmonosilane reacts with alcohols to form

esters of the type $C_6H_4Br \cdot Si(OR)_3$, which react with magnesium to form organo-metallic derivatives of little value for synthetic purposes. The *methyl* ester, $C_6H_4Br \cdot Si(OMe)_3$, has b. p. $136^\circ/13.5$ mm., $D_4^{15.5}$ 1.3525, D_4^{20} 1.3493, n_D 1.50791, n_D 1.51210 and n_D 1.52296 at 16.5° ; *ethyl* ester, b. p. $149-150^\circ/12$ mm., $D_4^{16.6}$ 1.2276, D_4^{20} 1.2244, n_D 1.48872, n_D 1.49247, n_D 1.50206 at 15.4° ; *propyl* ester, b. p. $175-176^\circ/14$ mm., $D_4^{18.8}$ 1.1564, D_4^{20} 1.1553, n_D 1.48144, n_D 1.48497, n_D 1.49386, n_D 1.50129 at 16.6° ; *isobutyl* ester, b. p. $190-191^\circ/14$ mm., $D_4^{17.2}$ 1.0949, D_4^{20} 1.0923, n_D 1.47531, n_D 1.47865, n_D 1.48698, and n_D 1.49424 at 14.9° (all densities are reduced to vacuum standard).

The magnesium compound of *p*-bromophenyltriethylmonosilane (*loc. cit.*) reacts badly with formaldehyde, smoothly with acetaldehyde (not paraldehyde), and tolerably well with higher aldehydes to form alcohols of the type $SiEt_3 \cdot C_6H_4 \cdot CHR \cdot OH$; the *ethanol* has b. p. $173-174^\circ/14.5$ mm., $D_4^{19.5}$ 0.9601, D_4^{20} 0.9596, n_D 1.51404, n_D 1.51822, n_D 1.52885, n_D 1.53810 at 17.2° ; the *propanol* has b. p. $185^\circ/16.5$ mm., $D_4^{17.0}$ 0.9603, D_4^{20} 0.9575, n_D 1.51243, n_D 1.51661, n_D 1.52734 at 18.0° ; the *n-butanol* has b. p. $199-201^\circ/21$ mm., D_4^{14} 0.9546, D_4^{20} 0.9491, n_D 1.50373, n_D 1.50754, n_D 1.51737; the *isobutanol* has b. p. $190-192^\circ/18$ mm., $D_4^{17.5}$ 0.9535, D_4^{20} 0.9512, n_D 1.50820, n_D 1.51212, n_D 1.52231 at 19.2° . By heating with fuming hydrochloric acid in a sealed tube at 90° , the ethanol gives a good yield of triethylsilicol, b. p. $70.5^\circ/16.5$ mm., $D_4^{19.7}$ 0.8650, D_4^{20} 0.8647, n_D 1.43393, n_D 1.43639, n_D 1.44228, n_D 1.44675 at 16.5° .

The magnesium compound of *p*-bromophenyltriethylmonosilane reacts with silicon tetrachloride in ethereal solution to form *trichloro-p-triethylsilylphenylmonosilane*, $SiEt_3 \cdot C_6H_4 \cdot SiCl_3$, b. p. $173-176^\circ/13.5$ mm., a colourless, highly refractive oil which has an offensive odour, fumes in air, and is at once hydrolysed by water. It reacts with magnesium ethyl bromide in ether to form *bis-p-triethylsilylbenzene*, $C_6H_4(SiEt_3)_2$, b. p. $195-196^\circ/16.5$ mm., $D_4^{17.6}$ 0.8989, D_4^{20} 0.8967, n_D 1.50555, n_D 1.50942, n_D 1.51945, n_D 1.52788 at 15.7° , a colourless, mobile, not unpleasantly odorous liquid, which is converted by bromination in the presence of an iron catalyst into *p*-dibromobenzene and bromotriethylmonosilane.

The interaction of magnesium *p*-bromophenyl bromide and phenyltrichloromonosilane in ether leads to the formation of *phenyl-p-bromophenyldichloromonosilane*, $C_6H_4Br \cdot SiPhCl_2$, b. p. $199-200^\circ/14$ mm., $D_4^{18.5}$ 1.5019, D_4^{20} 1.5005, n_D 1.60294, n_D 1.60921, n_D 1.62531, n_D 1.63953 at 19° , which is converted by ethyl alcohol into the *diethoxy*-compound, $C_6H_4Br \cdot SiPh(OEt)_2$, b. p. $201^\circ/17$ mm., $D_4^{21.5}$ 1.2474, D_4^{20} 1.2488, n_D 1.54525, n_D 1.55031, n_D 1.56322, n_D 1.57467 at 19° , and *bisethoxyphenyl-p-bromophenyldisiloxane*, $(C_6H_4Br \cdot SiPh \cdot OEt)_2O$, b. p. $317-318^\circ/20$ mm., D_4^{22} 1.3350, D_4^{20} 1.3369, n_D 1.57867, n_D 1.58437, n_D 1.59895, n_D 1.61146 at 18.6° . *Phenyl-p-bromophenyldiethylmonosilane*, $C_6H_4Br \cdot SiPhEt_2$, b. p. $203-203.5^\circ/13.5$ mm., $D_4^{19.7}$ 1.2156, D_4^{20} 1.2153, n_D 1.57794, n_D 1.58351, n_D 1.59781, n_D 1.61035 at 17.9° , and *phenyl-p-ethylphenyldiethylmonosilane*, $C_6H_4Et \cdot SiPhEt_2$, b. p. $169-170^\circ/14$ mm., $D_4^{19.0}$ 0.98403, D_4^{20} 0.98310, n_D 1.55716, n_D 1.56225.

n_D 1.57559, n_D 1.58713 at 16.8°, are obtained by the interaction of magnesium ethyl bromide and phenyl-*p*-bromophenyldichloromonosilane in ethereal solution, the product after distillation of the ether being heated at about 140° for three hours and then decomposed in the usual manner. Similarly, the product from magnesium ethyl bromide and trichloro-*p*-bromophenylmonosilane, after being heated at 180° for ten hours and then decomposed, yields *p*-ethylphenyltriethylmonosilane, b. p. 117—118°/18 mm., $D_4^{18.2}$ 0.8969, D_4^{20} 0.8950, n_D 1.50272, n_D 1.50671, n_D 1.51697, n_D 1.52583 at 20.7°. C. S.

Organic Lead Compounds. VIII. Mixed Lead Aryl Alkyls of the Type $PbArR_3$. GERHARD GRÜTTNER and GERTRUD GRÜTTNER (*Ber.*, 1918, 51, 1293—1298).—Such substances are obtained in accordance with the equation $PbR_3X + MgArX \rightarrow PbArR_3 + MgX_2$, where X is a halogen atom; the diaryl hydrocarbons which are formed as by-products can be removed by freezing or by fractional distillation. Lead aryl trialkyls are colourless, refractive, faintly odorous oils which in the presence of air and in diffuse daylight do not decompose in the course of many months. They decompose above 200° with the separation of lead, and by treatment with bromine in ether at -75° lose the aromatic group, and sometimes also an alkyl group to a slight extent, lead trialkyl bromides and lead dialkyl dibromides being formed. The latter is the main product in the case of lead benzyl triethyl.

The following are described. *Lead phenyl trimethyl*, b. p. 104°/13 mm., D_4^{27} 1.7342, D_4^{20} 1.7376, n_D 1.5753, n_D 1.5816, n_D 1.5988, n_D 1.6138 at 23.7°; *lead p-tolyl trimethyl*, b. p. 118—119°/13 mm., D_4^{20} 1.6826, $D_4^{21.5}$ 1.6812, n_D 1.5672, n_D 1.5732, n_D 1.5895, n_D 1.6039 at 20.0°; *lead o-tolyl trimethyl*, b. p. 117.5—118°/13 mm., $D_4^{21.4}$ 1.7395, D_4^{20} 1.7408, n_D 1.5734, n_D 1.5793, n_D 1.5954, n_D 1.6095 at 21.4°; *lead phenyl triethyl*, b. p. 135°/12 mm., $D_4^{21.1}$ 1.5920, D_4^{20} 1.5931, n_D 1.5698, n_D 1.5757, n_D 1.5917, n_D 1.6057 at 21.1; *lead p-tolyl triethyl*, b. p. 154.0°/13 mm., $D_4^{24.8}$ 1.5237, $D_4^{22.0}$ 1.5262, D_4^{20} 1.5281, n_D 1.5629, n_D 1.5686, n_D 1.5842, n_D 1.5979 at 22.0°; *lead o-tolyl triethyl*, b. p. 153.5°/13 mm., $D_4^{21.6}$ 1.5839, D_4^{20} 1.5853, n_D 1.5682, n_D 1.5740, n_D 1.5897, n_D 1.6035 at 21.5°; *lead benzyl triethyl*, b. p. 149—150.5°/13 mm., D_4^{23} 1.5374, $n_D^{21.4}$ 1.5843, appears to decompose slightly during distillation, some dibenzyl being formed.

Lead α-naphthyl triethyl loses naphthalene at its b. p. 176°/13 mm. *Lead benzyl trimethyl* decomposes at 124°. C. S.

Organic Lead Compounds. IX. Lead Triphenyl Haloids. GERHARD GRÜTTNER (*Ber.*, 1918, 51, 1298—1303).—An ethereal suspension of lead tetraphenyl in ether reacts with bromine at about -75° to form essentially a mixture of unchanged material and lead diphenyl dibromide, only about 10% of lead triphenyl bromide being formed. This result is doubtless to be attributed to the easy solubility of the monobromide and the sparing solubility of lead tetraphenyl, in consequence of which the first, when formed, is more readily attacked than the latter. When pyridine

at -50° is used instead of ether (compare Krause, A., 1918, i, 415), an almost quantitative yield of *lead triphenyl bromide*, PbPh_3Br , colourless needles, m. p. 166° , is obtained. It is converted into the *iodide*, PbPh_3I , pale yellow prisms, m. p. 142° , by aqueous potassium iodide, and into the *oxide* by cold 10% aqueous alkali hydroxide. The oxide is converted quantitatively into the *chloride*, PbPh_3Cl , colourless needles or prisms, m. p. 206° , by 15% hydrochloric acid at the ordinary temperature, and from a concentrated alcoholic solution of the latter, hydrogen sulphide precipitates the *sulphide*, $(\text{PbPh}_3)_2\text{S}$, as a white precipitate. C. S.

Physiological Chemistry.

The Consumption of Oxygen and Production of Carbon Dioxide in the Blood of Dogs. I. L. BERZELLER (*Biochem. Zeitsch.*, 1918, **90**, 294—301).—Sterile blood was kept under mercury or paraffin at 38° , and when fresh, and after keeping for various intervals, the oxygen and carbon dioxide were estimated by Barcroft's method. The production of carbon dioxide was generally found to be greater than the oxygen consumption. Similar experiments were carried out in the presence of dextrose. Here, again, there was no direct relationship between oxygen consumption and carbon dioxide production. There was a much larger oxygen consumption and carbon dioxide production than in normal blood.

S. B. S.

Analysis of Blood Gases. II. Hæmoglobin as an Indicator. The Theory of Indicators. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1918, **90**, 305—336).—There is a discontinuity of the curve expressing the amount of carbon dioxide taken up by the blood (hæmolysed by saponin freezing, etc.) plotted against the carbon dioxide tension. This discontinuity does not follow the ordinary laws of mass action, but begins when $p_{\text{H}} = 7.0$, at which point one molecule of carbon dioxide is taken up by one molecule of hæmoglobin. This indicates that when $p_{\text{H}} > 7.0$ the hæmoglobin molecules carry a negative charge, which they lose as soon as $p_{\text{H}} = 7$. When $p_{\text{H}} = 6.39$, a second point of discontinuity is reached in the curve, which indicates that at this point the hæmoglobin molecules acquire a positive charge. These phenomena are explained in reference to the charges carried by the colloidal particles, and not by the laws of mass action, for the position of the bends in the curve depends also on the presence of other ions than those of hydrogen. Univalent anions and cations, and bivalent cations exert no influence on the position of the bend; tervalent anions shift the position of the first bend from $p_{\text{H}} = 7.00$ to $p_{\text{H}} = 6.80$,

and are without action on the position of the second bend. Tervalent cations also exert a strong influence on the position. The application of these facts to the use of hæmoglobin as an indicator is discussed.

S. B. S.

The Influence of Narcotics on the Permeability of Blood-corpuscles for Dextrose and Carbamide. GERTRUD KATZ (*Biochem. Zeitsch.*, 1918, **90**, 153—165).—The entrance of dextrose into human blood corpuscles is not inhibited by the narcotics heptyl alcohol and thymol. The entrance of carbamide into ox-corpuscles is delayed by thymol.

S. B. S.

The Part Played by Acid in Carbohydrate Metabolism. III. Acid and the Glycogen of the Muscles. H. ELIAS and E. SCHUBERT (*Biochem. Zeitsch.*, 1918, **90**, 229—243).—The glycogen content of the muscles of dogs' legs differs, the right from the left, by about 2—3% in the mean. Interarterial injection of lactic acid over several hours does not reduce to any appreciable extent the amount of glycogen; the muscle glycogen appears to be far more resistant to external stimuli than does the liver glycogen.

S. B. S.

Salivary Amylase. I. A Preliminary Experimental Study of its Stability in Saliva. ROLLIN C. MYERS and LEONARD C. SCOTT (*J. Amer. Chem. Soc.*, 1918, **40**, 1713—1716).—Salivary amylase in sterilised saliva without preservative is found to be relatively stable for a year. The relative stability may vary from practically no change to that of more than 50% of its former amylolytic activity, the variation depending probably on slight differences in the composition of the saliva.

The causes which lower the stability of salivary amylase in saliva are not solely the degrading action of bacteria, mould spores, yeast plants, and special preservatives. The inherent chemical weakness of the enzyme molecule must be taken into account, which weakness may be increased by the maintenance of temperatures from 18° to 30°, by diffused light and by compounds in the saliva.

Salivary amylase in saliva is relatively stable for a year when preserved with toluene, thymol, and chloroform. Toluene has the least destructive action on the enzyme, and thymol and chloroform follow in order.

Saliva may be kept for two and a-half years under the ordinary laboratory conditions without preservative, and may still show a form of amylolytic activity.

H. W.

The Presence of Food Accessories in Urine, Bile, and Saliva. A. M. MUCKENFUSS (*J. Amer. Chem. Soc.*, 1918, **40**, 1606—1611).—As a result of a series of experiments on pigeons with acute symptoms of polyneuritis, the author is led to the conclusion that the antineuritic vitamine is probably present in comparatively small quantity in clean, fresh, filtered bile from the

bladder of the ox, and that traces of it appear to be present in fresh filtered human urine. H. W.

Fischer's Theory of Water Absorption in Œdema. W. J. CROZIER (*J. Amer. Chem. Soc.*, 1918, **40**, 1611—1612. Compare Fischer, A., 1918, i, 129, 130, 131; Henderson and Cohn, *ibid.*, i, 316).—The author has carried out a series of experiments on the intracellular acidities in the tissues of three species of sponges, one echinoderm, and a nudibranch mollusc. The observations made increase the difficulties in the way of accepting Fischer's conception of water metabolism, since they indicate a range of intracellular acidities, in animal tissues, within which it is known that no significant protein swelling occurs, and since they show that an intracellular acidity even remotely approaching that at which significant swelling might be possible is irreversibly associated with natural death. H. W.

The Storage and Excretion of Arsenic after Administration by Salvarsan in Serum and Water. HANS BERGMANN (*Biochem. Zeitsch.*, 1918, **90**, 348—360).—The author investigated the rate of excretion of arsenic excreted in the urine of man after administration of neosalvarsan in serum (human) and in aqueous solutions. In the latter case the excretion is much greater. Experiments are quoted which tend to show that the salvarsan undergoes chemical change more rapidly in aqueous solution than in serum. A series of experiments is also described, in which the accumulation of arsenic in the organs of rabbits after administration of salvarsan was investigated. They tend to indicate a greater accumulation after administration of the drug in serum. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

A Bacterium present in Water and in Bitter Wines which is capable of Dehydrating Glycerol. A New Reaction for Glycerol. E. VOISENET (*Ann. Inst. Pasteur*, 1918, **32**, 476—510. Compare A., 1914, i, 462).—The new bacterium, termed *Bacillus amaracrylus*, is related to *B. coli* and *B. typhosus*, but is not pathogenic. When cultivated in dextrose solution, it forms carbon dioxide and hydrogen, like *B. coli*, but it does not form indole from tryptophan. Inoculation of a medium containing glycerol with the new bacterium results in the production of acraldehyde, which is its characteristic reaction. H. W. B.

The Inter-relationship of certain processes in Metabolism of *Bacillus coli communis*. FRITZ VERZER (*Biochem. Zeitsch.*, 1918, **91**, 1—45).—Three main series of investigations were

instituted: (1) The influence of certain poisons on the different processes, (2) the influence of one metabolism product on the formation of others, (3) the regulation of the formation of a product by its own accumulation. The processes investigated were (*a*) gas formation from dextrose, (*b*) acid formation from dextrose and lactose, (*c*) indole formation, (*d*) reducing action on dyes, (*e*) multiplication of the bacteria.

(1) Protoplasmal poisons, phenol, formaldehyde, and mercuric chloride inhibit all the processes in about the same concentration. Crystal-violet shows slight inhibition of gas formation, but strong inhibition of reducing processes. The respiratory poison, potassium cyanide, inhibits strongly gas formation and still more strongly reduction processes and indole formation in concentrations in which the acid formation is not affected. The narcotic, chloroform, inhibits respiration, but not as strongly as potassium cyanide; in contrast to the latter, it also inhibits acid formation. Alcohol acts, but less strongly, like chloroform. The author draws the conclusion that the only really essential vital process is the formation of acid from dextrose.

(2) From the study of the presence of acid on indole formation it was found that the latter is inhibited entirely by the presence of acids, and is only normally produced from proteins or peptones by the bacteria in the absence of dextrose; scission of this by the bacteria produces acid to inhibit indole formation.

(3) The influence of the presence of acids and alkalis on the further formation of acids by the bacteria was investigated. It was found that when the acid in the culture medium reached a certain concentration, further formation of acid was inhibited, and also further formation of carbon dioxide, and multiplication of bacteria. If sugar insufficient to produce the amount of acid necessary for inhibitions is present, alkali formation sets in, until the medium attains a slightly alkaline reaction, when further formation of alkali is inhibited. The formation takes place only in presence of oxygen. From acid (except formic acid) no gas is formed either after reaching its maximum concentration or during formation of alkali. Inhibition of oxidation causes a compensatory increased production of acid.

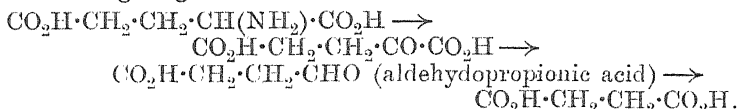
S. B. S.

Phytochemical Reductions. XIII. Asymmetrical Reduction. Conversion of Racemic Valeraldehyde (*dl*- α -Methylbutaldehyde) into *l*-Amyl Alcohol. C. NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1918, **90**, 388—394).—The amyl alcohol produced from *dl*- α -methylbutaldehyde by a sugar-yeast fermentation mixture is laevorotatory.

S. B. S.

The Method of Formation of Succinic Acid in Nature. III. Conversion of Aldehydopropionic Acid into Succinic Acid by Yeast. C. NEUBERG and M. RINGER (*Biochem. Zeitsch.*, 1918, **91**, 131—136).—By means of maceration juice, and in absence of air, aldehydopropionic acid can be converted into succinic acid.

The conversion of glutamic acid into succinic acid follows, therefore, the following stages:



All these stages except the first, which takes place, as far as investigations have gone, only in the living cell, can be accomplished by purely enzymatic reactions.

S. B. S.

Physiological Investigation of a New Yeast which Flourishes in Tanning Liquors. TÔICHI ASAI (*J. Coll. Sci. Imp. Univ. Tokyo*, 1918, **39** (7), 1—42).—The new yeast, designated *Mycoderma tannica*, forms dark brown or brownish-black spots on leather undergoing the tanning process. The isolated yeast can be cultivated in a solution containing dextrose or lævulose or other carbohydrate, and an ammonium salt or amino-acid as a source of nitrogen. It does not readily grow in a dilute pure tannin solution, but when dextrose and aspartic acid are also present, rapid decomposition of the tannin occurs, owing to the excretion of tannase into the surrounding medium. The growth of the yeast is attended by the production of small quantities of alcohol and carbon dioxide, indicating the presence of zymase. Addition of tannin to the medium increases slightly the alcoholic fermentation.

H. W. B.

Kinetics of the Cell-free Fermentation [by Zymase].

OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 185—225).—The addition of sugar to an extract of dried yeast containing zymase, but free from cells, is succeeded by a period of quiescence, during which no sign of fermentation is observable. The interval which elapses between the addition of the sugar and the first appearance of fermentation is termed the "induction period." The duration of the induction period is determined by various factors; it is shorter for sucrose than for either dextrose or lævulose; it can be shortened by previously warming the sugar solution with disodium hydrogen phosphate or by grinding the dried yeast with glass powder. The presence of a small amount of hexose phosphate abolishes the induction period.

The rate of fermentation is dependent on the amount of free phosphate present. Increasing the amount of disodium hydrogen phosphate reduces the rate at which the velocity of fermentation increases, but the maximum velocity eventually attained is higher than in the absence of free phosphate until a certain maximum amount of the phosphate is reached; further addition of the phosphate then reduces the maximum velocity of fermentation attainable. The addition of other salts, such as sodium chloride, produces similar effects on the velocity of fermentation. The free phosphate functions, therefore, as a salt as well as exerting its specific zymase-activating action.

Hexose phosphate exerts an accelerating action on fermentation in proportion to its concentration, due to the decomposition of the ester itself. Fermentation is accelerated also by the addition of co-ferment in the form of boiled yeast juice; the extent to which it is affected depends on the concentration, and not on the absolute quantity of the co-ferment present in relation to zymase.

The inhibiting influence of narcotics on the fermentation of dextrose by zymase is somewhat intensified by the addition of salts.

H. W. B.

Rôle of the Phosphate in Alcoholic Fermentation.

HANS EULER and S. HEINTZE (*Zeitsch. physiol. Chem.*, 1918, 102, 252—261).—The esterification of phosphoric acid by dried yeast in the presence of a protoplasmic poison, such as phenol, is related to the amount of water remaining in the yeast after the drying process. The maximum esterification is observed when dried yeasts containing from 10 to 15% of moisture are employed. Increasing the quantity of yeast used in the individual experiments appears to occasion a much greater increase in the amount of hexose phosphate produced.

H. W. B.

Fumaric Acid Fermentation of Sugar. C. WEHMER (*Ber.*, 1918, 51, 1663—1668).—*Aspergillus fumigatus* smoothly ferments relatively large quantities of sugar, yielding, in addition to a little citric acid, fumaric acid in the free state; the solution turns Congo-paper blue and dissolves calcium carbonate. Oxygen is necessary and, for continuous fermentation, calcium carbonate. Thus 20 grams of sugar (20% solution) and 2.87 grams (dry weight) of *Aspergillus fumigatus* dissolve 15 grams of calcium carbonate and produce about 33 grams of calcium salts consisting chiefly of the sparingly soluble normal calcium fumarate, but containing also varying quantities of the easily soluble hydrogen fumarate, about 4% of calcium citrate, and the calcium salt of another, unidentified acid. The sugar is fermented completely, and 60—70% of it is converted into acids. The optimum temperature is about 22°, the maximum about 30°.

C. S.

Behaviour of Organic Compounds in Plants. X. G.

CIAMICIAN and C. RAVENNA (*Gazzetta*, 1918, 48, i, 253—304. Compare A., 1918, i, 473).—The first part of this paper, dealing with the action of certain compounds on the germination and development of plants, has been already abstracted.

The second part describes further investigations on the oxidation of organic compounds by the agency of enzymes contained in spinach leaves. The results of experiments in an atmosphere of carbon dioxide show that the disappearance of certain substances in an atmosphere of oxygen as a result of the action of such enzymes is due to an oxidation process.

In an atmosphere of carbon dioxide, saligenin is converted into the polyanhydride saliretin, this change being effected more

promptly by apple pulp than by spinach leaves. Ethyl alcohol and mannitol are not sensibly oxidised. Acetaldehyde, which undergoes little auto-oxidation in an atmosphere of oxygen, is not affected by the presence of the enzyme. The oxidation of acetone to formic and acetic acids under the influence of light is catalysed by the presence of the enzyme. Of the three amino-acids examined, glycine, alanine, and asparagine, only the last is oxidised by the enzyme in an atmosphere of oxygen, no change occurring in carbon dioxide. Cinnamic acid is not oxidised at the double linking, only minimal traces being transformed into the isomeric *isocinnamic* acid; this isomerisation does not occur in carbon dioxide. Of the alkaloids examined, caffeine and strychnine remain unchanged, whereas morphine, quinine, and cinchonine are largely oxidised.

The enzymes of spinach leaves are also able to determine certain other reactions. Thus, in oxygen, dextrose is completely oxidised, probably to carbon dioxide, whilst in carbon dioxide it yields a substance giving dextrose on hydrolysis with acid. Further, in either oxygen or carbon dioxide, tartaric acid undergoes change, partly into a compound yielding tartaric acid under the action of emulsin.

The results of the experiments described in the third part of the paper show that, when inoculated into the living plant (maize), pyridine and nicotine are partly eliminated through the leaves, the transformation of further quantities by the plant being also indicated, but not definitely proved.

T. H. P.

The Influence of Immersion in certain Electrolytic Solutions on Permeability of Plant Cells. MAUD WILLIAMS (*Ann. Bot.*, 1918, **32**, 591—599).—Cells of London Pride (*Saxifraga umbrosa*) petioles, after immersion in solutions of certain electrolytes, were found to be permeable to a 0.2% solution of ferric chloride, the entrance of the ferric chloride being indicated by formation of a blue colour with the tannin contained in these cells. The time of immersion in a given solution necessary to produce this abnormal permeability varied with the electrolyte and its concentration. In the cases of aluminium and potassium chlorides, and potassium and barium nitrates, the results obtained could be expressed approximately by the equation

$$\log T = K - A(\log C + 1),$$

where T is the time of immersion in the solution of the electrolyte needed to produce the abnormal permeability, C is the concentration in gram-mols. per litre, K is an independent constant, and A a constant depending on the electrolyte used. Abnormal permeability with respect to ferric chloride was not always accompanied by permeability to the rose-coloured pigment frequent in the sap of the cells.

W. G.

The Occurrence of Melezitose in a Manna from the Douglas Fir. C. S. HUDSON and S. F. SHERWOOD (*J. Amer. Chem. Soc.*, 1918, **40**, 1456—1460).—A sample of manna from

the Douglas fir yielded about 50% of pure crystalline melezitose, and there is evidence that it contained sucrose and some reducing sugar, probably a mixture of dextrose with a smaller quantity of levulose. The composition of the sample of dry manna was approximately: melezitose 75–83%, sucrose 2.9%, reducing sugars 11.5%. At present, the only other known natural source of melezitose in any quantity is the Tarkestan manna (Tarandjabiné), which is, however, considerably inferior to the Douglas fir product in point of yield.

H. W.

Occurrence of Allantoin in the Rhizome of *Symphytum officinale* and other Borraginaceæ. ALFRED VOGL (*Pharm. Post.*, 1918, 51, 181–184; from *Chem. Zentr.*, 1918, ii, 36).—Large quantities of allantoin crystals, in the form of monoclinic prisms, are found in the rhizome of *Symphytum officinale*. The author has also succeeded in identifying allantoin crystals in the sections of the rhizome and has determined their distribution in the tissue. Crystallisation in the sections is best effected by pouring on them alcohol containing acetic acid (20%), covering with a cover-glass, and sealing with paraffin. The allantoin content of the rhizome of *S. officinale* varies with the time of year; it is at a maximum from autumn to early spring, at a minimum in the height of summer. The rhizomes of *S. tuberosum*, *S. cordatum*, *S. caucasicum*, and other *Borraginaceæ* appeared to be free from allantoin, possibly owing to unfavourable supply of material.

H. W.

Action of Ammonium Salts on Plants. I. H. G. SÜDERBAUM (*Kunigl. Landtbruks-Akad. Handlingar*, 1917, 56, 537–561; from *Physiol. Abstr.*, 1918, 3, 351).—This paper reports experiments with small grains and potatoes grown in pots, using ammonium salts as fertilisers; sodium nitrate was used in part for control purposes. The favourable influence of these salts on the total yield ranks as follows: diammonium hydrogen phosphate, ammonium carbonate, sulphate, nitrate, sodium nitrate, ammonium chloride. The phosphate gave a crop four times as large as an equivalent amount of the sulphate; the chloride proved very disadvantageous. Up to a certain limit, the addition of ammonium sulphate gave a progressively increased yield, but when the limit had been passed, there was a marked decrease. The adverse action of an excess of the salt was not the same in the case of each plant. Rye and potatoes were least sensitive in this respect, and wheat and barley most so, whilst oats occupied an intermediate position. Where there is neither soil acidity nor a deficiency of calcium, ammonium sulphate may be used to advantage in the field, as the amount applied in practice does not reach the limit where toxicity manifests itself.

H. W. B.

Organic Chemistry.

Methane. WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1918, **22**, 529—575).—A summary is given of the work which has been published, from all sources, on the physical and chemical properties of methane, and a number of important problems requiring investigation are enumerated. [See *J. Soc. Chem. Ind.*, 1919, 35A.] E. H. R.

Organic Chemical Reagents. II. Amylene. *tert*-Amyl Alcohol. ROGER ADAMS, O. KAMM, and C. S. MARVEL (*J. Amer. Chem. Soc.*, 1918, **40**, 1950—1955).—Dehydration of primary alcohols by sulphuric acid generally proceeds less satisfactorily as the molecular weight of the alcohol increases. Amylene may, however, be satisfactorily obtained from commercial amyl alcohol under the following conditions. Amyl alcohol (1.5 litres) and concentrated sulphuric acid (100 c.c.) are heated to vigorous boiling under a reflux condenser in which the water is maintained at such a temperature (60—90°) as to allow a considerable amount of vapour to distil out of the apparatus; the top of the condenser is connected with a second, efficiently cooled condenser, attached so as to permit downward distillation. The heating requires a maximum time of about eight hours. At first, water and amyl alcohol pass over, whilst subsequently amylene distils. The distillate is washed with sodium hydroxide to remove sulphur dioxide and the amylene isolated by fractionation. It appears to consist of β -methyl- Δ^{α} -butylene and β -methyl- Δ^{β} -butylene containing only a negligible amount of γ -methyl- Δ^{α} -butylene. The residue in the original flask contains amyl alcohol and *iso*amyl ether, which are recovered by distillation with steam and subsequent fractionation. About 250 c.c. of amylene, 400 c.c. of *iso*amyl ether, and 500 c.c. of amyl alcohol are obtained from 1500 c.c. of the latter.

Larger amounts of amylene are more conveniently obtained by the pyrogenic-catalytic method, using aluminium oxide as catalyst at 500—540°. A suitable electrically heated furnace is fully described. The general procedure is similar to that indicated by Ipatieff (*A.*, 1903, i, 593). The yield of amylene is 70—80% of the theoretical, and the product is about 98—99% pentene. The catalyst retains its activity over lengthy periods.

tert-Amyl alcohol is prepared by the gradual addition of amylene to a mixture of concentrated sulphuric acid and ice. The product is diluted with ice-water (after removal of any unchanged amylene), rendered alkaline with sodium hydroxide, and distilled. 275—300 Grams of a product, b. p. 100—103°, may be obtained from 325 grams of amylene. H. W.

Geometrical Isomerism. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 605—610).—The inconsistencies which are introduced

by the attempts to explain the existence of the *cis*- and *trans*-isomerides of ethylenic compounds of the type $(A,B)C=C(A,B)$ by the theories of Werner and Stark are pointed out. All such theories set out to explain how the existence of the double bond prevents free rotation of the two doubly-linked carbon atoms about the line joining their centres. The explanations of Werner and of Stark are shown to be inconsistent with the hypotheses which they put forward as to the nature of the atoms and the mechanism by which the atoms are linked together. The author points out that it is hopeless to attempt to base an hypothesis of the structure of the benzene ring, for example, on theories which are inadequate to explain the mechanism of the double bond. S. I. L.

Derivatives of Trihalogeno-*tert*.-butyl Alcohols. II. The Propionic and Butyric Esters of Tribromo-*tert*.-butyl Alcohol (Brometone). T. B. ALDRICH (*J. Amer. Chem. Soc.*, 1918, **40**, 1948—1950. Compare Aldrich and Beckwith, A., 1917, i, 77).— β -Tribromomethylpropan- β -ol is converted into the corresponding *propionate*, white crystals, m. p. 27°, by the action of propionyl chloride. The similarly prepared *butyrate* is an oil, b. p. 144—145°/13—14 mm. Both are comparatively inactive pharmacologically, due probably to their not being decomposed into soluble constituents having a typical physiological action and are rather slowly absorbed. H. W.

Glyceryl Methyl Ether Dinitrate (α -Methylin Dinitrate). DAVID TREVOR JONES (T., 1919, 115, 76—81).

The Action of Sodium Hydroxide on Carbon Monoxide, Sodium Formate, and Sodium Oxalate. MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1779—1786).—It has been shown (this vol., ii, 63) that fused sodium oxide is very active in effecting oxidations. It is now demonstrated that at 410—430°, carbon monoxide in contact with fused sodium hydroxide is oxidised to carbon dioxide, an equivalent amount of hydrogen being produced at the same time. Sodium formate when fused with sodium hydroxide at 275°, a temperature much below its decomposition temperature, is oxidised almost quantitatively to carbon dioxide in a very short time, an equivalent amount of hydrogen also being formed. Sodium oxalate is similarly oxidised at 290°. In both these cases, it is the water present in the fusion, catalysed by the sodium hydroxide, which is the effective oxidising agent. It is held that the general reaction involving the replacement of the carboxyl group by hydrogen in alkali fusions, for example, in the formation of benzene from sodium benzoate, involves simultaneous oxidation and reduction by the oxygen and hydrogen of water. [See also *J. Soc. Chem. Ind.*, 1919, February.] E. H. R.

Quinonoid Character of Maleic Anhydride. PAUL PFEIFFER and THEODOR BÖTTLER (*Ber.*, 1918, **51**, 1819—1829. Compare Pratt and Perkins, A., 1918, i, 167).—Maleic anhydride is related

to furan in the same manner as quinone to benzene; it may therefore be regarded as a quinone of furan, and, in the present communication, evidence is adduced to show that the formal analogy is reproduced in its properties.

A characteristic property of quinones is their ability to yield more or deeply coloured molecular compounds with aromatic hydrocarbons, amines, phenols, and phenol ethers (A., 1914, i, 551; 1917, i, 205); this property is shared by maleic anhydride, which, although yielding colourless solutions in benzene, toluene, or *m*-xylene, gives coloured solutions with durene, hexamethylbenzene, naphthalene, 2:4:5:2':4':5'-hexamethylstilbene, *o*-tolyl methyl ether, and quinol and dimethylaniline. The influence of substituents in the molecule of the solute and solvent, respectively, is similar in the cases of *p*-benzoquinone and of maleic anhydride. Thus, methylation in the quinone molecule exerts a hypsochromic action on the colour of the quinhydrone; similarly, solutions of citraconic anhydride are less intensely coloured than corresponding solutions of maleic anhydride. Methylation in the benzenoid component produces a deepening of colour in the cases of *p*-benzoquinone and of maleic anhydride. The introduction of an *ortho*-condensed benzene nucleus has a similar influence in each instance, as is proved by the comparison of α -naphthaquinone with *p*-benzoquinone on the one hand and of phthalic anhydride with maleic anhydride on the other. The deepening in colour caused by the introduction of halogen atoms into the quinone molecule is remarkably characteristic; the same effect is produced in the anhydrides, as proved by examination of bromomaleic, dibromomaleic, and tetrachlorophthalic anhydrides. Attempts to isolate the additive compounds of maleic anhydride or its bromo- or methyl derivatives in the crystalline state were not successful, but similar substances were readily obtained from tetrachlorophthalic anhydride and durene (long, pale yellow needles) and hexamethylstilbene (orange-coloured, shining leaflets, m. p. 183—184°), respectively.

The effect of alteration in the structure of the anhydride has also been investigated. Succinic anhydride yields colourless solutions in all the media mentioned above, whilst the solutions of itaconic anhydride are much less deeply coloured than those of citraconic anhydride. When dissolved in dimethylaniline, itaconic anhydride is gradually isomerised to citraconic anhydride. On passing from the anhydride to the corresponding acid or its esters, the quinonoid character is largely lost and the solutions are colourless or less intensely coloured, as is shown at the instances of maleic and dibromomaleic acids, of methyl fumarate, and of methyl tetrachlorophthalate. The substance, $\text{CO}_2\text{H}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CHO}$, scarcely possesses any quinonoid characteristics, but these are more marked with *trans*-dibenzoyl ethylene. γ -Pyrone and the ketones of the distyryl ketone series are less nearly related to quinone than is maleic anhydride; the former yields completely colourless solutions, whilst those of the latter only show faint colorations.

It was to be expected that imides of the type of maleimide

would also show quinonoid characteristics; this is actually the case, but solutions of citraconanil and tetrachlorophthalimide are less deeply coloured than those of citraconic and tetrachlorophthalic anhydrides.

Maleic, citraconic, phthalic, and tetrachlorophthalic anhydrides do not exhibit halochromic phenomena when treated with concentrated sulphuric acid, trichloroacetic acid, or tin tetrabromide. Further investigation of this problem has led to the conclusion that the carbonyl groups of the substances which yield quinhydrones and of typical halochromic compounds must differ markedly in their chemical nature. H. W.

Oxidation of Organic Compounds by Silver Oxide.

ROBERT BEHREND and KARL DREYER (*Annalen*, 1918, 416, 203—225).—It has long been known that many acids and alcohols are oxidised by silver oxide, but hitherto a systematic investigation has not been made of the relation between the constitutions of substances and their tendency to oxidation or of the nature and quantity of the products of oxidation. The present paper deals with these points in the case of the simpler, hydroxylic aliphatic compounds. In order that a substance may be oxidised by silver oxide in alkali hydroxide or ammoniacal solution, it must contain a $\text{:CH}\cdot\text{OH}$ (or CO or C[OH]_2) group combined with two $\cdot\text{CH}_2\cdot\text{OH}$, two $\text{:CH}\cdot\text{OH}$, or two $\cdot\text{CO}_2\text{H}$ groups, or with any two of these three groups. Tartronic, tartaric, dihydroxytartaric, glyceric, mucic, saccharic, and gluconic acids, dextrose, glycerol, and mannitol are thus oxidised. For oxidation in neutral or acid solution, it suffices that the $\text{:CH}\cdot\text{OH}$ group shall be combined with a carboxyl group and also with H , CH_2 , or CH_3 . Glycollic, lactic, malic (and also formic) acids are thus oxidised. Propylene glycol, ethyl alcohol, isopropyl alcohol, and oxalic acid suffer little or no oxidation. In alkali hydroxide solution, substances of the group first mentioned are oxidised rapidly and completely; the rate of oxidation is accelerated, but the relative quantities of the products of oxidation are unaffected by an increased concentration of the alkali hydroxide. In ammoniacal solution, silver oxide oxidises the alkali salts of the acids completely in fifty minutes at 90° . The acids are more easily oxidised in the form of alkali salts than in the form of ammonium salts. An excess of ammonia or of ammonium salt retards the oxidation.

The products of oxidation in alkaline solution contain at most two atoms of carbon, and are never obtained in simple molecular proportions. All the substances with the exception of glycerol yield carbon dioxide as one of the products of oxidation in acid or in alkaline solution. Formic acid is a product of oxidation in alkaline solution, and then only if the oxidisable substance contains a $\text{:CH}\cdot\text{OH}$ group united with a $\text{:CH}\cdot\text{OH}$ or $\cdot\text{CH}_2\cdot\text{OH}$ group as well as with a $\text{:CH}\cdot\text{OH}$, $\cdot\text{CH}_2\cdot\text{OH}$, or $\cdot\text{CO}_2\text{H}$ group. Formic acid may be an intermediate product of oxidation in acid solution, but in such circumstances it undergoes further oxidation. Oxalic

acid is almost always the chief product of oxidation in alkaline solution; in neutral or acid solution, it is formed in much smaller quantity. In neutral solution, malic acid yields malonic acid, and lactic acid and propylene glycol yield acetic acid. C. S.

Tartronic Acid. ROBERT BEHREND and AUGUST PRÜSSE (*Annalen*, 1918, **416**, 233—239).—Tartronic acid has been prepared by eleven investigators, who record eight different m. p.'s between 145° and 185°. The correct value appears to be 156—158° (decomp.). C. S.

Preparation of Gulonolactone. F. B. LA FORGE (*J. Biol. Chem.*, 1918, **36**, 347—349).—To a solution of 150 grams of xylose in 300 c.c. of water, 30 grams of hydrocyanic acid are added, and then a few drops of ammonium hydroxide. The reaction commences at once, and is completed in about six hours at 35°. Slightly more than one equivalent (55 grams) of sulphuric acid diluted with a small amount of water is added to the solution, which is then concentrated at once to a viscous syrup. Hydrolysis of the nitrile takes place, and on cooling and keeping, the lactone crystallises out. The yield after recrystallisation from 60% alcohol amounts to 55 to 60% of the weight of xylose used. H. W. B.

Crystallography and Optical Properties of Three Aldopentoses. EDGAR T. WHERRY (*J. Amer. Chem. Soc.*, 1918, **40**, 1852—1858).—The optical properties of the crystals of the three sugars α -*d*-lyxose, α -*d*-xylose, and β -*d*-arabinose enable them to be readily distinguished, and a determinative table is given for this purpose. For the determination of the refractive indices by the immersion method, suitable mixtures of turpentine oil (n 1.47), clove oil (n 1.53), and α -bromonaphthalene (n 1.66) are used.

α -*d*-Lyxose forms monoclinic, probably sphenoidal, crystals, $a:b:c=1.608:1:1.828$; $\beta=62^\circ 10'$; mean refractive index, n 1.541; D^{20} 1.545; molecular refraction, M 30.60.

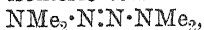
α -*d*-Xylose, rod-shaped, monoclinic, probably sphenoidal, crystals, $a:b:c=1.655:1:1.776$; $\beta=62^\circ 55'$; n 1.536; D^{20} 1.525; M 30.67.

β -*d*-Arabinose, rhombic, probably sphenoidal, needles, $a:b:c=1.497:1:0.738$; n 1.568; D^{20} 1.605; M 30.61.

Lyxose and xylose are obviously very closely related crystallographically, and β -arabinose, although crystallising in a different system from the others, shows closely similar inter-facial angles, and the three sugars form an essentially isomorphous group. The molecular refractivities are all slightly lower than that calculated from the atomic refractivities, 31.2. The divergence is probably due to some peculiarity of molecular configuration. E. H. R.

Tetramethylammonium Azide. FRANK V. FRIEDLANDER (*J. Amer. Chem. Soc.*, 1918, **40**, 1945—1947).—*Tetramethylammonium azide*, NMe_4N_3 , is prepared by the gradual addition of a solution of tetramethylammonium iodide to an aqueous suspension of a slight excess of silver azide. The crystals belong to the tetragonal system ($a:c=1.07245$). It is a fairly

stable substance which does not explode when struck with a hammer, when ground in a mortar, or when dropped on a hot plate; the dry salt begins to decompose at about 125°. Attempts to transform it into the isomeric tetramethyltetrazone,



have been unsuccessful up to the present.

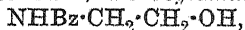
H. W.

Glycosine. ROBERT BEHREND and HERMANN KÖLLN (*Annalen*, 1918, 416, 230—233).—In addition to glyoxaline, very small quantities of glycosine are obtained by the action of ammonia on glyoxal. The yield of glycosine is considerably increased by the following procedure. In a tall cylinder are placed 20 c.c. of nitric acid, D 1.4, containing ten to fifteen drops of fuming nitric acid, 25 c.c. of water, and 25 c.c. of paraldehyde, the three liquids being introduced with as little intermixture as possible. The cylinder is immersed in water, the level of which is higher than that of the liquids in the cylinder. When the liquids have intermixed after some days and the evolution of gas has ceased, the mixture is repeatedly evaporated with water to remove volatile acids as completely as possible, and the residual syrup is diluted to 50 c.c. with water, producing an approximately 20% solution of glyoxal. One-half of this solution is evaporated until the temperature is 120°. 25—30 grams of ammonium acetate which has been heated at this temperature are gradually added, the resulting brownish-black liquid is dried at 100—110° and treated with water. The black residue of crude glycosine is dried in air and then at 70°, dissolved in warm 35% hydrochloric acid (which is added drop by drop), the solution is diluted with water, boiled with animal charcoal (free from iron), filtered after keeping for twenty-four hours in the warm, the brown filtrate is boiled again with animal charcoal, and the colourless filtrate is neutralised by ammonia, whereby glycosine is obtained in 42.5% yield.

A modification of Pinner's method of preparing trichlorolactic acid from chloral is described.

C. S.

β -Aminoethyl Alcohol and its Derivatives. SIGMUND FRÄNKEL and MARTHA CORNELIUS (*Ber.*, 1918, 51, 1654—1662).—The following derivatives have been prepared to facilitate the identification of the amino-alcohol. β -Benzoylaminoethyl alcohol,



prepared by boiling an alcoholic solution of the dibenzoyl derivative with the quantity of solid potassium hydroxide calculated to eliminate one benzoyl group, forms colourless leaflets, m. p. 66—67°. β -Acetylaminoethyl acetate, $\text{NHAc} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OAc}$, b. p. 103°/0.049 mm., is obtained by boiling β -aminoethyl alcohol with acetic anhydride. β -Acetylaminoethyl alcohol, prepared from the amino-alcohol and acetyl chloride at 0°, forms colourless needles, m. p. 63—65°. β -Naphthalenesulphonylaminoethyl alcohol, $\text{C}_{10}\text{H}_7 \cdot \text{SO}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, asbestos-like crystals, m. p. 86—87°, is obtained by adding *N*-sodium hydroxide to an ethereal solution

of β -naphthalenesulphonyl chloride (2 mols.) and β -aminoethyl alcohol (1 mol.), and subsequently acidifying the aqueous solution. *β -m-Nitrobenzoylaminoethyl m-nitrobenzoate*,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, colourless needles, m. p. 152—153°, obtained by heating β -aminoethyl alcohol (1 mol.) and *m*-nitrobenzoyl chloride on the water-bath, is reduced by the calculated quantity of tin and hydrochloric acid to *β -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride*, $\text{C}_{16}\text{H}_{17}\text{O}_3\text{N}_3\cdot 2\text{HCl}$, crystals, m. p. 232°. *β -p-Nitrobenzoylaminoethyl p-nitrobenzoate*, yellow needles, m. p. 188—189°, and *β -p-aminobenzoylaminoethyl p-aminobenzoate*, crystals, m. p. 206°, are obtained by similar methods. *β -Phenylcarbamidoethyl phenyl-carbamate*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NHPh}$, colourless crystals, m. p. 190—191°, is obtained by adding phenylcarbimide drop by drop to cold β -aminoethyl alcohol, and then heating the mixture in a sealed tube at 100°. *β -Aminoethyl hydrogen sulphate*, $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}_3\text{H}$, colourless crystals, m. p. 230°, is obtained from the amino-alcohol and fuming sulphuric acid in a freezing mixture.

β -Glycylaminoethyl glycine,

$\text{NH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$, obtained by adding chloroacetyl chloride (2 mols.) to a chloroform solution of β -aminoethyl alcohol (1 mol.) at 0° in the presence of lead carbonate, warming the mixture for a moment on the water-bath, and, after the cessation of the reaction and evaporation of the chloroform, treating the residual yellow syrup with concentrated aqueous ammonia, is a yellow syrup which is converted by the Schotten-Baumann method into *β -hippurylaminoethyl hippurate*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NHBz}$, colourless leaflets, m. p. 144°.

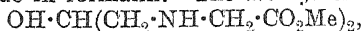
Dicarbaminoethyl carbonate, $\text{CO}\left\langle\begin{smallmatrix} \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \\ \text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O} \end{smallmatrix}\right\rangle\text{CO}$, crystals, m. p. 88—90°, is obtained by the prolonged action of carbonyl chloride on β -aminoethyl alcohol in chloroform solution in the presence of lead carbonate.

β -Aminoethyl alcohol in very dilute solution responds to the iodoform test. By treating an aqueous solution of the amino-alcohol with sodium nitrite and Ehrlich's reagent (2% alcoholic *p*-dimethylaminobenzaldehyde and dilute hydrochloric acid), an intense canary-yellow coloration is produced which is not destroyed by warming or by the addition of aqueous ammonia or potassium hydroxide.

β -Benzoylaminoethyl alcohol, *β -m-aminobenzoylaminoethyl m-aminobenzoate hydrochloride*, and *β -p-aminobenzoylaminoethyl p-aminobenzoate* are not anæsthetics. C. S.

β -Hydroxytrimethylenediglycine. HUGO KRAUSE (*Ber.*, 1918, 51, 1556—1571. Compare *A.*, 1918, i, 156, 337).— β -Hydroxytrimethylenediglycine has D_4^{25} 1.348 by the swimming method. Its solution in formalin or water produces on a pine shaving a greenish-yellow, but not very intense, coloration; the reaction may

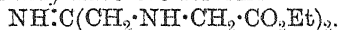
be used as a sensitive method of detecting glycine. The coloration is destroyed by alkali hydroxide or carbonate and by ammonia. Esters of β -hydroxytrimethylenediglycine are obtained by the action of aqueous sodium hydroxide on a solution of the glycine ester hydrochloride in formalin. The *methyl* ester,



a viscous, colourless liquid still containing 10% of formaldehyde, D¹⁵ 1.18, is obtained in only 19% yield, but the *ethyl* ester is more readily obtained. When pure, it has b. p. 140—150°/16 mm. (partial decomp.), D¹⁵ 1.150, and a molecular weight in benzene or naphthalene corresponding with its formula. It is comparatively stable towards sodium hydroxide, but is decomposed quantitatively by cold dilute hydrochloric acid, yielding methyl alcohol, formaldehyde, and ethyl glycine hydrochloride.

When the ethyl ester (84% purity) is heated at 16—18 mm., the distillate, apart from formaldehyde and unchanged ester, consists of a pale yellow oil, b. p. 200°/16 mm., which appears to be *ethyl methyleneglycine*, $\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, or *ethyl ethylenediglycine*, $\text{C}_2\text{H}_4(\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, more probably the former.

In the expectation of preparing the amide, ethyl β -hydroxytrimethylenediglycine was heated with alcoholic ammonia at 68—70° for twenty-four hours, but the chief product was a *substance*, $\text{C}_{11}\text{H}_{21}\text{O}_4\text{N}_3$, which may have the formula



The silver salt, $\text{C}_9\text{H}_6\text{O}_3\text{N}_3\text{Ag}$, previously described (*loc. cit.*), can also be prepared by dissolving glycine in 30% formaldehyde solution in the cold, neutralising this solution immediately with 4*N*-potassium hydroxide (phenolphthalein as indicator), and adding 20% silver nitrate solution. It is decomposed in aqueous suspension by hydrogen sulphide, yielding formaldehyde and glycine. The acid corresponding with the silver salt is therefore probably *N*-hydroxymethylglycine, $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

C. S.

Comparisons and Similarities: Water and Ammonia.

G. CIAMICIAN (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 141—146). —Attention is directed to the chemical analogy between OH_2 and NH_3 , between $\cdot\text{OH}$ and $\cdot\text{NH}_2$, and between $\cdot\text{O}$ and $\cdot\text{NH}$ (compare Angeli, A., 1910, ii, 844, 948; 1915, i, 847). Such analogy is clearly shown in the relation between $\text{C}\cdot\text{O}$ and $\text{C}\cdot\text{NH}$, the ready oxidation of cyanides to cyanates corresponding with that of carbon monoxide to carbon dioxide, and the reduction by zinc of cyanic acid with that of carbon dioxide. These relations are further rendered evident by the following series of equations: $\text{CO}_2 + \text{H}_2\text{O} = \text{CO}(\text{OH})_2$; $\text{CO}_2 + \text{NH}_3 = \text{OH}\cdot\text{CO}\cdot\text{NH}_2$; $\text{O}\cdot\text{C}\cdot\text{NH} + \text{NH}_3 = \text{CO}(\text{NH}_2)_2$; $\text{C}(\cdot\text{NH})_2 + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$; $\text{C}(\cdot\text{NH})_2 + \text{ROH} = \text{OR}\cdot\text{C}(\cdot\text{NH})\cdot\text{NH}_2$; $\text{C}(\cdot\text{NH})_2 + \text{NH}_3 = \text{NH}\cdot\text{C}(\text{NH}_2)_2$. The polymerisation of cyanamide to dicyanodiamide corresponds with the synthesis of guanidine and its derivatives, the two tautomeric forms of cyanamide being regarded as reacting: $\text{C}(\cdot\text{NH})_2 + \text{CN}\cdot\text{NH}_2 = \text{NH}_2\cdot\text{C}(\cdot\text{NH})\cdot\text{NH}\cdot\text{CN}$. Other similar analogies are recorded.

T. H. P.

Formation of Carbamide from Ammonium Carbonate and Related Substances. FR. FICHTER, HEINRICH STEIGER, and THEOPHIL STANISCH (*Verh. Schweiz. Nat. Ges.*, 1916, **28**, ii, 66—103; from *Chem. Zentr.*, 1918, ii, 444—446).—In a previous communication (Fichter, Stutz, and Grieshaber, A., 1913, i, 713), the formation of carbamide by the electrolysis of ammonium carbamate was attributed to the intermediate production of formamide by the action of hydroxylamine on ammonium carbamate; this view can no longer be maintained, since direct experiment shows that ammonium carbamate is not reduced by hydroxylamine. On the other hand, carbon dioxide reacts with hydroxylamine in the same manner as with ammonia, giving, according to conditions, hydroxylamine carbonate or the dihydroxylamine salt of hydroxycarbamic acid, $\text{OH}\cdot\text{NH}\cdot\text{CO}_2\text{H}, 2\text{NH}_2\cdot\text{OH}$. The experiments on the electrolysis of ammonium carbamate solution (*loc. cit.*) have therefore been repeated, the same solution being used as in previous experiments, but every care being taken to keep the anode and cathode solutions separate by enclosing the electrodes in porous pots immersed in a trough, all vessels containing the same solution. The results show that carbamide is produced exclusively at the anode, but no trace of a corresponding reduction product, such as formic acid or formamide, could be detected at the cathode. Under the experimental conditions, Liebig's method of detecting carbamide is unsuitable, but Fosse's method (A., 1914, ii, 756) gives trustworthy results, is not affected by the presence of ammonium salts; and allows the isolation of carbamide by the action of alcoholic hydrogen chloride on the dioxanthylcarbamide.

Attempts have also been made to effect the oxidation of ammonium carbamate to carbamide by purely chemical means; hydrogen peroxide or calcium permanganate gives small but distinctly recognisable quantities of carbamide. Oxidation may also be effected by ozone, either by leading ozonised oxygen into ammonium carbamate solution or over powdered ammonium carbonate, or by mixing ozonised oxygen, ammonia, and carbon dioxide. The yield depends on the concentration of ammonia and the temperature. The chemical and electrochemical oxidations have the transformation of ammonia into ammonium nitrate as a common feature; also, the local increase in temperature caused by the reaction is sufficient to cause a purely thermal transformation of ammonium carbamate into carbamide.

The general explanation of the equilibrium between ammonium carbamate and carbamide is that the former passes into the latter by loss of a molecule of water. This, however, is opposed to the law of mass action; the change is more probably represented by the scheme: $\text{NH}_5\cdot\text{CO}_2\text{NH}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$. Direct experiment shows that the rate of formation of carbamide is increased by water in the early stages of the reaction, as is required by the above hypothesis. The authors are therefore led to the conclusion that normal ammonium carbonate is the

actual source of carbamide; since, however, the presence of water has an effect disadvantageous to the carbamide in the final equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, it is advisable to operate with substances containing the components of ammonium carbonate, but having less water, such as ammonium carbamate. At the temperature of the reaction, the small quantity of hygroscopic moisture is sufficient to start the conversion of the carbamate into carbonate, and as soon as the latter commences to be transformed into carbamide, water is liberated in amount sufficient to complete the hydration of the carbamate. In the anhydrous condition, ammonium carbamate is more stable than the carbonate; in the presence of water, however, it becomes unstable, and, above a certain temperature, is incapable of existence. In the region above 135° , there is only the equilibrium between ammonium carbonate and carbamide, in which the latter is favoured by further rise of temperature; below 135° , on the other hand, the complex equilibrium of the first scheme exists. The maximum yield obtained at 135° thus finds a simple explanation. The equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, has been investigated at 125° , 100° , 78° , and $37\text{--}38^\circ$, and the combined effects of temperature and dilution are explicable from the point of view of the complex equilibrium scheme. Lowering of temperature renders the carbamate and the carbamide more stable; increase in the quantity of water acts in the opposite direction in each case. According to the preponderance of one or the other factors, the following effects may be observed at temperatures below 135° with a constant molecular ratio of carbamate to water: (1) the second portion of the scheme may be so far favoured that the yield of carbamide is increased, since the amount of water suffices to convert a larger proportion of carbamate into carbonate in spite of the actual increased stability of the former; (2) the yield may remain constant, since the increase in stability of the carbamate balances the increased tendency to formation of carbamide; (3) the increased stability of the carbamate is not counterbalanced by the amount of water, and the yield of carbamide sinks. All three possibilities have been experimentally realised. Free ammonia favours the carbamide in the equilibrium, $(\text{NH}_4)_2\text{CO}_3 \rightleftharpoons \text{CO}(\text{NH}_2)_2 + 2\text{H}_2\text{O}$, in the absence of water, but is without influence in presence of the latter.

H. W.

Acetylmethylcarbamide. ROBERT BEHREND and HANS ODENWALD (*Annalen*, 1918, 416, 228—229).—Fifty-nine grams of acetamide (1 mol.) are dissolved in 88 grams of bromine (0.55 mol.), a 20% solution of potassium hydroxide (56 grams; 1 mol.) is added, the solution is heated on the water-bath until it becomes yellow and is no longer alkaline, and is then cooled, when acetylmethylcarbamide crystallises. Further quantities can be obtained from the mother liquor, the total yield being 75% of the theoretical. With even a slight excess of alkali, the yield falls to zero. C. S.

Substitution in Aromatic Compounds. H. J. PRINS (*Chem. Weekblad*, 1918, 15, 571—580).—It has been shown in an earlier paper (*ibid.*, 98) that substitution in aromatic compounds begins by addition to a carbon atom of the ring, followed by reaction with the hydrogen atom attached to that carbon atom; the reactivity of the hydrogen atom depends, therefore, in the first place, on the degree of unsaturation of the atom to which it is attached, as is true also in the case of alcohols and amines. Since unsaturation is distributed over the whole nucleus, addition can obviously occur at more than one carbon atom. The analogy with alcohols and amines is shown, not only in the carbon atoms of the nucleus, but in oxygen or nitrogen atoms in side-chains attached to the nucleus, and substitution can be brought about in all these cases by the same catalysts.

Substitution may be not only direct, but indirect also, as in the case of chloroacetanilide; the reaction here is unimolecular, and may be ascribed to a disturbance of the equilibrium between the energy of the atoms (atom-energy) and the energy of combination between the atoms (link-energy). Substitution occurs, then, in the first place at the least saturated carbon atom, but this may not yield the most stable system, and the substituting group may finally take up a different position.

The entry of any substituent X into the benzene ring must cause a change in the relation between atom-energy and link-energy, both in the substituent and in the nucleus. Two cases may arise. In the first, in which the link-energy between X and C₁, the carbon atom to which X becomes attached, is greater than that between C₁ and the hydrogen atom displaced; the atom-energy of C₁ is therefore reduced, and to restore this as far as possible, the link-energy between C₁ and its neighbours, C₂ and C₆, is reduced, with the consequence that the link-energy between C₂ and C₃ and between C₃ and C₄ is increased (C₄ and C₅ being the neighbours of C₂ and C₃ remote from C₁), and that between C₄ and C₅ and C₅ and C₆ is diminished; C₄, therefore, by the diminution of its link-energy, receives an increase of atom-energy, and is therefore rendered more reactive. The effect of introducing X, therefore, is to make the para-carbon atom more reactive. In the second case, in which the link-energy between C₁ and the substituent is less than between C₁ and hydrogen, the redistribution of energy causes an increase in the atom-energy of C₄ and C₅, that is, of the carbon atoms in the meta-position.

The fact that a substituent which directs a second substituting group to the meta-position also causes a reduction in the velocity of substitution is taken to indicate that the atom-energy of the atoms of the substituted nucleus is less than that of the atoms of the unsubstituted benzene ring itself, and hence it follows that the introduction into the ring of a group which directs to the meta-position causes the transformation of atom-energy into link-energy throughout the ring as a whole.

It is shown that substitution in the benzene ring cannot be explained by the assumption of a conjugated system, as attempted by Böeseken (A., 1912, i, 430) and by Holleman (*Chem. Weekblad*, 1913, 10, 615, 618), without postulating many other conditions.

S. I. L.

Pyrogenic Acetylene⁺Condensations. V. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1918, 51, 1571—1587. Compare A., 1917, i, 313).—In addition to the substances previously identified in the product of the pyrogenic condensation of acetylene, *o*-xylene (identified as *o*-phthalic acid) and indene have been detected and the presence of mesitylene and ψ -cumene confirmed. Durene and isodurene could not be detected. The methylthiophen obtained by the condensation of acetylene, methane, and hydrogen sulphide (*loc. cit.*) is proved to be α -thiotolen, and thionaphthen has been found in the product of the condensation of acetylene and hydrogen sulphide. A complete list is given of all the products obtained by pyrogenic acetylene condensations.

Hydrindene brominated in the cold in the presence of a little iodine yields 4:5:6:7-tetrabromohydrindene, $C_6Br_4 < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} > CH_2$, needles, m. p. 200° (which is converted into tetrabromophthalic acid by oxidation), but, brominated in boiling chloroform, yields 1:2:3-tribromohydrindene, feathery crystals, m. p. 134°, which yields phthalic acid by oxidation, and is also obtained by the further bromination of indene dibromide.

About 0.5 c.c. of aniline was obtained when the vapour of 3 litres of benzene mixed with ammonia was passed during twenty-four hours through a tube heated at 550° initially and at 700° finally; aniline could not be detected if the temperature was maintained at 550° throughout. [See also *J. Soc. Chem. Ind.*, 1919, 35A.]

C. S.

The Optically Active neoMethylhydrindamines. JOSEPH WALTER HARRIS (T., 1919, 115, 61—67).

The Fusion of Sodium Hydroxide with Several Phenols and Sulphonic Acids. MATTLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, 40, 1786—1793).—A number of experiments were carried out in which sodium benzene-sulphonate was fused with sodium hydroxide at temperatures of 300—350° in a closed vessel in presence or absence of air, the gaseous contents of the tube being analysed before and after the experiments. It was found that when the fusion was carried out in presence of air, a considerable quantity of hydrogen was formed and a much smaller quantity of methane or other gaseous hydrocarbon. At the same time, some of the oxygen originally present disappeared, the volume ratio of hydrogen formed to oxygen used up being approximately 1:2. When air is excluded from the fusion, however, no hydrogen or methane appears. It was found, working on comparatively large quantities of material, that by

carrying out the fusion in an atmosphere of nitrogen instead of air, the yield of phenol could be increased from 90% to 98% of the theoretical.

In the presence of free oxygen, secondary reactions evidently occur involving the absorption of oxygen, followed by an oxidation involving the elements of water. To determine whether any of the dihydroxy- or trihydroxy-benzenes are formed as secondary products, the fusion of all six of these with sodium hydroxide in presence or absence of air was studied. In the case of five of them, hydrogen was formed in presence, not in absence of air. In the case of hydroxyquinol, much hydrogen is evolved even in absence of air, and also considerable quantities of methane. It is not considered that any of these can be the direct cause of hydrogen formation in the benzenesulphonate fusion.

Sodium hydroxide does not bring about catalytic oxidation of the dihydroxybenzenes, of pyrogallol, of β -naphthalenesulphonic acid, or phenylglycine-*o*-carboxylic acid. With sodium anthraquinone- β -sulphonate, however, oxidation occurs in absence of oxygen, with formation of free hydrogen. E. H. R.

The Miscibility of Phenol and Alkaline Solutions. RENÉ DUBRISAY, TRIPIER, and TOQUET (*Compt. rend.*, 1918, 167, 1036—1038).—The coefficient of reciprocal miscibility of phenol and water steadily increases with the addition of alkali hydroxides to the water. Curves are given for sodium hydroxide at concentrations varying from $N/20$ to $N/3$. The action of the alkaline earth hydroxides is similar, but less marked. On the other hand, acids and salts of the strong acids cause a diminution in the coefficient, and the same holds good for the alkali carbonates.

W. G.

Aromatic Derivatives of Orthosulphurous Acid. M. M. RICHTER (*Annalen*, 1918, 416, 291—304. Compare A., 1917, i, 24).—The attempt to prepare aryl sulphates in the same way as aryl sulphites (*loc. cit.*) by means of sulphuryl chloride and pyridine failed, chlorinated liquid products being obtained. Phenyl sulphate is obtained indirectly by dissolving phenyl sulphite in concentrated sulphuric acid with cooling and pouring the solution into water. The amorphous precipitate obtained separates from formic acid solution in plates with blunted angles, m. p. 288° (decomp.; rapidly heated) or 280 — 282° (decomp.; slowly heated). The substance is regarded as a double salt of diphenyl sulphate (1 mol.) and diphenyl sulphite (2 mols.) having the formula $\text{SO}_2[\text{O}\cdot\text{S}(\text{OPh})_2]_2$, that is, it is a *sulphate of triphenyl-orthosulphurous acid*. It is easily soluble in formic, sulphuric, and phosphoric acids, in methyl sulphate and in alkali hydroxides and carbonates, ammonia and alkali sulphides, dissolves slightly in warm methyl or ethyl alcohol and in boiling water, and is insoluble in all other common solvents. It is converted by alcoholic hydrochloric acid at 70° into the *chloride of triphenyl-orthosulphurous acid*, $\text{S}(\text{OPh})_2\text{Cl}$, long, prismatic needles, m. p. 256° (decomp.). and in dilute potassium hydroxide solution by a solution of pyridine

hydrochloride containing an excess of pyridine into *triphenylorthosulphurous acid*, $\text{OH}\cdot\text{S}(\text{OPh})_3$, an amorphous powder, m. p. 233° . The last substance is amphoteric. Its acidic character is weaker than that of carbonic acid, whilst its basic properties are such that a hot 50% alcoholic solution has an alkaline reaction towards litmus. The three phenyl groups are not eliminated by hydrolysing agents. By treating an alcoholic suspension of the acid with the requisite acid, the *bromide*, $\text{S}(\text{OPh})_3\text{Br}$, needles, m. p. $241\text{--}242^\circ$ (decomp.), *iodide*, short needles, m. p. $194\text{--}195^\circ$ (reddening), *nitrate*, hair-like needles, m. p. $160\text{--}161^\circ$ (decomp.), *acetate*, waxy mass, and *picrate*, yellow mass, are obtained. *Ethyl triphenylorthosulphite*, $\text{OEt}\cdot\text{S}(\text{OPh})_3$, amorphous powder, m. p. 244° (decomp.), is obtained from the chloride and alcoholic sodium ethoxide.

The *sulphate*, $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_6\text{H}_4\text{Me})_3]_2$, crystals, m. p. 296° (decomp.), prepared from di-*o*-tolyl sulphite, and the corresponding *sulphate*, m. p. 315° (decomp.), prepared from di-*m*-tolyl sulphite, are obtained in the same way as the phenyl analogue; the latter yields *tri-m-tolylorthosulphurous acid*, amorphous powder, m. p. 267° (decomp.), by treatment with pyridine hydrochloride as above.

The colourless, amorphous *sulphate*, m. p. 232° (decomp.), obtained by pouring a solution of dithymyl sulphite in concentrated sulphuric acid into water, is regarded as a mixed anhydride of sulphuric, dithymylorthosulphurous, and trithymylorthosulphurous acids, $(\text{C}_{10}\text{H}_{13}\cdot\text{O})_3\text{S}\cdot\text{O}\cdot\text{SO}_2\cdot\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_2\cdot\text{OH}$. It is soluble in alcohol, but by treating its solution in aqueous-alcoholic potassium hydroxide with alcoholic sulphuric acid, a *sulphate*, $\text{SO}_2[\text{O}\cdot\text{S}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3]_2$, amorphous powder, m. p. $280\text{--}281^\circ$ (decomp.), is precipitated, which is insoluble in alcohol. The insoluble sulphate yields *trithymylorthosulphurous acid*, amorphous powder, m. p. $274\text{--}275^\circ$ (decomp.), by the pyridine hydrochloride method, whilst the soluble sulphate, by treatment with alcohol and the requisite acid, yields the *chloride*, $\text{SCl}(\text{O}\cdot\text{C}_{10}\text{H}_{13})_3$, amorphous powder darkening at $295\text{--}300^\circ$ without melting, *bromide*, small crystals, decomp. $330\text{--}340^\circ$, *iodide*, crystals, and *nitrate*, small, rectangular plates blackening at $285\text{--}290^\circ$ without melting.

C. S.

Thiophenol in Synthetic Phenol. G. CAPPELLI (*Gazzetta*, 1918, **48**, ii, 107—113).—The repulsive odour exhibited by some samples of synthetic phenol is sometimes attributed to the presence of thiophen in the benzene used in the manufacture. The author shows that such odour is due to a small proportion of thiophenol, formed from particles of sodium benzenesulphonate which, during the fusion with alkali, escape contact with the latter and undergo deoxidation at the surface of the iron in the manner observed by Stenhouse (*Annalen*, 1866, **140**, 284; 1869, **149**, 42). The phenol may be freed from this impurity by fusing it, adding a little alcohol to keep it liquid, and then adding, per kilo. of phenol, about 50 c.c. (more, if continued formation of precipitate shows it to be neces-

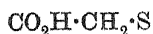
sary) of 10% alcoholic mercuric chloride solution. The excess of mercuric chloride is eliminated by leaving the clear liquid for a couple of days in contact with copper turnings or foil; the mercury deposited on the latter may be recovered by distillation. Fractional distillation of the decanted solution gives: (1) below 179°, water and alcohol, and (2) at 179—183°, pure phenol with its characteristic odour. T. H. P.

Organic Salts of Bivalent Chromium. G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 87—89; *Gazzetta*, 1918, 48, ii, 148—150).—The greyish-green salt obtained by Calcagni (A., 1913, i, 1154) either from chrome alum and sodium salicylate or from chromic hydroxide and salicylic acid, and regarded by him as a chromous compound, is probably a salt of trivalent chromium in which also the phenolic hydroxyl groups take part in the salt-formation. All other chromous salts of organic acids, including those now described by the author, are red.

Chromous salicylate, $C_6H_4 \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} Cr \cdot 3H_2O$, prepared by reducing chrome alum solution with zinc and hydrochloric acid and adding sodium salicylate solution free from air, forms small, red crystals, but rapidly oxidises and becomes greenish-grey in the air.

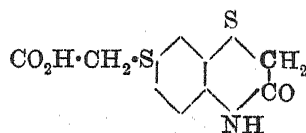
Chromous propionate, $2(C_3H_5O_2)_2Cr \cdot H_2O$, was also prepared and analysed, and the butyrate and valerate prepared. T. H. P.

Nitro-2:4-phenylenedithioglycolic Acid and Some of its Colouring Derivatives. C. FINZI and N. BOTTIGLIERI (*Gazzetta*, 1918, 48, ii, 113—122).—The authors have prepared the nitro-derivative of *m*-phenylenedithioglycolic [*m*-phenylenedithiolacetic] acid, and as this yields on reduction, not an amino-acid, but a ketothiazine derivative, the conclusion is drawn that the nitro-group enters the benzene nucleus in the ortho-position to one of the substituents. The sulphone corresponding with the nitro-compound undergoes ring-closure on reduction still more easily, the resultant compound being quite analogous to Clausz's sulphazone (A., 1912, i, 389), and being hence termed sulphazon-sulphonacetic acid. This acid has been coupled with various diazo-compounds, the derivatives thus obtained being of different colours and serving as substantive dyestuffs for silk.



4-Nitro-*m*-phenylenedithiolacetic acid (annexed formula), obtained from *m*-phenylenedithiolacetic acid and nitric acid, forms slender, yellow needles, m. p. 174°.

2-Keto-2:3-dihydrothiazine-6-thiolacetic acid (annexed formula),

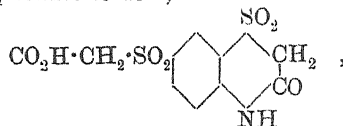


obtained by reducing the previous compound, forms tufts of silky, white needles. m. p. 210°; its sodium salt (+3H₂O) was prepared and analysed.

4-Nitro-*m*-phenylenedisulphonacetic acid, $NO_2 \cdot C_6H_3(SO_2 \cdot CH_2 \cdot CO_2H)_2$, prepared by the action of hydrogen per-

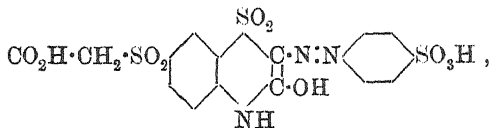
oxide on the nitro-acid, forms long, white needles, m. p. 199° (decomp.). On reduction with tin and hydrochloric acid, it yields

Sulphazon-6-sulphonacetic acid,

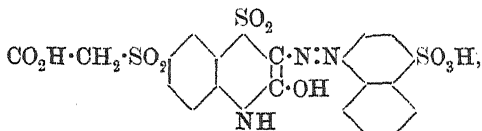


which forms white, mammillary masses of slender needles, m. p. 219° (decomp.).

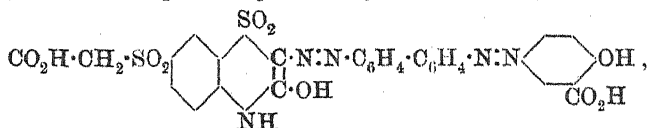
p-Sulphobenzeneazosulphazon-6-sulphonacetic acid,



obtained by condensing the preceding acid with diazobenzene-sulphonic acid, forms small needles of the colour of chromic anhydride. At 40—50° in aqueous solution, it is fixed directly on silk, giving a brilliant orange-yellow colour stable against soap and light; wool fixes it with more difficulty, but assumes a stable, yellow coloration. *4-Sulphonaphthaleneazosulphazonacetic acid*,



dyes silk an old-gold yellow stable against soap and light. *Salicylic-acid-p-azodiphenyl-p'-azosulphazonsulphonacetic acid*,

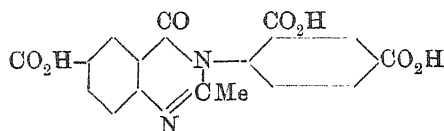


forms a brownish-black colouring matter almost insoluble in water, and directly colours silk yellow with an olive-green tinge.

T. H. P.

4-Aminoisophthalic Acid and its Derivatives. RUDOLF WEBSCHIEDER, HANS MALLE, ALFRED EHRLICH, and ROBERT SKUTEZKY (*Monatsh.*, 1918, **39**, 375—417).—4-Acetylaminoisophthalic acid is conveniently prepared by oxidising 4-aceto-mxylicide with a boiling aqueous solution of calcium permanganate; when rapidly heated, it becomes yellow at about 270°, melts at 295—296° (corr.; decomp.), immediately resolidifies, and then remains unchanged up to 350°; when slowly heated, decomposition frequently occurs without visible liquefaction. (The *calcium* salt

[+3H₂O] is described.) During the heating, one molecule of acid loses its acetyl group, and the residue reacts as an amine with a second molecule of acid, yielding thereby 4-keto-3-phenyl-2-methyl-3:4-dihydroquinazoline-6 : 2' : 4'-tricarboxylic acid (annexed



formula), m. p. 416° (corr.). [Ethyl ester, m. p. 332° (corr.) after sintering at 330°.]

The esters of 4-acetyl-aminoisophthalic acid were prepared by acetylation of

the corresponding esters of the amino-acid: methyl 4-acetyl-aminoisophthalate has m. p. 125—126°; 1-methyl 3-hydrogen 4-acetylaminoisophthalate melts at 218—219°; the corresponding normal and acid ethyl esters have m. p.'s 109—110° and 193·5—194·5° respectively. Attempts to esterify the acetylamino-acid by methyl alcohol and mineral acids led, as in the case of acetylaminoterephthalic acid (Wegscheider and Faltis, A., 1912, i, 463) to the deacetylation of the acid.

4-Aminoisophthalic acid is most conveniently prepared from its acetyl derivative by esterifying the latter with methyl alcohol and mineral acid, and subsequent hydrolysis of the purified amino-ester so formed; it has m. p. 336—337° (corr.; decomp.). The dimethyl and diethyl esters have m. p.'s 131·5° and 79—80° respectively, whilst 1-methyl 3-hydrogen 4-aminoisophthalate and the corresponding ethyl ester melt at 224—225° (decomp.) and 216·5—218°. The acid behaves contrary to the usual rule, since it yields the same ester by treatment with mineral acid and methyl alcohol and by half-hydrolysis of the normal ester.

The methylation of the amino- and acetylamino-acids and their esters has been studied under varying conditions. 4-Dimethyl-aminoisophthalic acid is most conveniently prepared by treatment of the corresponding dimethyl ester with methyl sulphate at 100° and hydrolysis of the ester (m. p. 70°) with alcoholic potassium hydroxide; its m. p. depends greatly on the mode of heating. The silver salt is described. Methylation of the free acid is very incomplete either by the action of methyl sulphate on the dry potassium salt in the presence of potassium hydroxide solution or in the presence of water and barium carbonate. The use of methyl iodide and potassium hydroxide does not lead to better results. 4-Acetylaminoisophthalic acid is methylated with still greater difficulty, yielding small amounts of dimethylaminoisophthalic acid. Methyl sulphate does not act on dimethyl 4-acetylaminoisophthalate below 115°; at 120—124°, however, trimethyl 4-keto-3-phenyl-2-methyl-3 : 4-dihydroquinazoline-6 : 2' : 4'-tricarboxylate, m. p. 205·5°, is produced.

4-Acetylmethylaminoisophthalic acid is prepared by the action of methyl iodide on the sodium or, preferably, the potassium salt of dimethyl 4-acetylaminoisophthalate and subsequent hydrolysis with alcoholic potassium hydroxide solution; it forms colourless

needles, the m. p. of which depends on the mode of heating. 4-Methylaminoisophthalic acid has m. p. 297·5—298·5° (corr.) after decomposition at 296° when placed in a bath preheated to 293°; the corresponding dimethyl ester melts at 115°. 1-Methyl 3-hydrogen 4-methylaminoisophthalate, m. p. 238—239° (decomp.), is obtained by the partial esterification of 4-methylaminoisophthalic acid with methyl alcohol and hydrogen chloride. H. W.

Colour and Chemical Constitution. III. Derivatives of the Unknown op-Phenolphthalein. JAMES MOIR (*Trans. Roy. Soc. S. Africa*, 1918, 7, 123—127. Compare A., 1917, ii, 349, 557).—The preparation and absorption spectra of a number of phthalein derivatives containing one hydroxyl group in the *ortho*- and a second in the *para*-position to the central carbon atom are described. Thus phenol-*p*-cresolphthalein is obtained by heating a mixture of *p*-cresol and *p*-hydroxybenzoylbenzoic acid in the presence of zinc chloride. The following substances are prepared in a similar manner: op-phenolphthalein-*m*-carboxylic acid and its methyl ether, hydroxydiphenylphthalidicarboxylic acid, *m*-amino-op-phenolphthalein, the corresponding *m*-methylamino-derivatives and its ω -carboxylic acid, *m*-phenyl-op-phenolphthalein, and *m*-nitro-op-phenolphthalein. Attempts to prepare op-phenolphthalein by reduction of *m*-iodo-op-phenolphthalein did not yield the desired result, and further work in this direction was abandoned, since it was discovered that *p*-hydroxybenzoylbenzoic acid yields a phthalein-like substance when heated at above 200°, or at a lower temperature in the presence of concentrated sulphuric acid; this substance, which resembles phenolphthalein very closely, can also be obtained by heating phenolphthaleinoxime with a small quantity of sulphuric acid at above 200°, and it therefore appears probable that the so-called oxime is in reality the *p*-hydroxyanilide of *p*-hydroxybenzoylbenzoic acid.

It is possible to find a particular strength of alkali in which any phthalein gives a colourless solution in the cold, but which becomes coloured on heating to near the boiling point, and again fades on cooling and keeping. For ordinary phenolphthalein, the concentration of alkali is slightly above normal; tetraiodo-phenolphthalein requires a much weaker alkali, whilst α -naphtholphthalein requires about 2*N*-alkali.

Phenolphthalein-*o*-carboxylic acid is coloured faintly pink by ammonia and deep violet-pink by alkali hydroxide; as an indicator, it resembles thymolphthalein, but has a more favourable colour. The corresponding dicarboxylic acid is useful in proving the presence of definite caustic alkalinity at about *N*/100.

H. W.

Constitution of the Hydrazone of Benzaldehyde. J. SUREDA BLANES (*Anal. Fis. Quim.*, 1918, 16, 707—718).—The author summarises the evidence for and against the cyclical formula of Curtius for the aliphatic diazo-compounds, $RR'C \begin{smallmatrix} \diagup N \\ \diagdown N \end{smallmatrix}$, as com-

pared with the lineal formula, $RR \cdot C:N:N$, suggested by Angeli and later by Thiele.

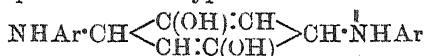
The easy oxidation of hydrazones to diazo-compounds suggests the investigation of the constitution of the former substances. The hydrazone chosen for preliminary examination is that of benzaldehyde, which on oxidation gives phenyldiazomethane. The alternative structures which may be assigned to benzaldehydehydrazone are: $CHPh \begin{smallmatrix} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix}$ and $CHPh:N \cdot NH_2$.

The following reactions establish the latter formula:

- (1) Benzaldehydehydrazone and phenylcarbimide,
 $CHPh:N \cdot NH_2 + CONPh = NPh \cdot CO \cdot NH \cdot N : CHPh$.
- (2) Benzaldehydehydrazone and phenylthiocarbimide,
 $CHPh:N \cdot NH_2 + SCNPh = NPh \cdot CS \cdot NH \cdot N : CHPh$.
- (3) Benzaldehydehydrazone and diphenylketen,
 $CHPh:N \cdot NH_2 + CPh_2 \cdot CO = CHPh_2 \cdot CO \cdot NH \cdot N : CHPh$.

The product of the last reaction forms white crystals insoluble in alcohol, ether, or benzene, slightly soluble in light petroleum and glacial acetic acid, m. p. 196° . These reactions are incompatible with the cyclical formula for benzaldehydehydrazone, and therefore the lineal formula must be assumed. W. S. M.

Anilinoquinones. HERMANN SUIDA and WILHELM SUIDA (*Annalen*, 1918, 416, 113—163).—The generally accepted view that anilinoquinones are always formed by the transformation of an additive compound of the type



into $NHAr \cdot C \begin{smallmatrix} & CO \cdot CH \\ & \diagup \quad \diagdown \\ CH \cdot CO \end{smallmatrix} > C \cdot NHAr$, with the removal of four atoms of hydrogen, which reduce two further molecules of the quinone, is found not to hold. In some cases, the reaction recognisably passes through the monoanilide. In the case of the simplest and most reactive components, monoanilides are smoothly formed in accordance with the equation $2C_6H_4O_2 + NH_2Ar = C_6H_5O_2 \cdot NHAr + C_6H_4(OH)_2$. The capacity of the group $\cdot CO \cdot CH : CH \cdot CO \cdot$ to form anilino-compounds must be connected in some way with the structure of the benzene nucleus, because maleic and fumaric esters and the *cis*- and *trans*-modifications of dibenzoyl ethylene, in which this group occurs, do not react in this way with aromatic amines.

Under the conditions of the authors' experiments, the following generalisations have been made. *p*-Benzoquinone in aqueous, faintly acetic acid solution yields with all pronouncedly basic primary and secondary aromatic amines anilinoquinones, predominantly and even sometimes exclusively monoanilinoquinones. The intensity of the reaction diminishes as the basic character of the amine is weakened by the entrance of acidic substituents. Thus the strongest bases (aniline and its homologues, diamines, etc.) yield mono- and di-anilides simultaneously, the weaker bases (secondary amines, nitroanilines, etc.) yield only monoanilides,

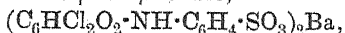
whilst the weakest bases do not react in aqueous solution. Toluquinone yields only monoanilides, and *s*-xyloquinone does not react.

In alcoholic solution, *p*-benzoquinone forms only dianilides; monoanilides are present in the mother liquor only when the basic component contains acidic substituents. Tolu- and naphthoquinones yield only monoanilides, and *s*-xyloquinone none.

The reactions also proceed in glacial acetic acid solution. Therefore by a suitable selection of the solvent and of the temperature it is possible to make a quinone react once or twice with an amine, or a monoanilinoquinone to react with a different base, producing a mixed dianilinoquinone.

The following new derivatives of *p*-benzoquinone have been prepared: 5-anilino-2- α -naphthylamino-, $C_{23}H_{16}O_2N_2$, yellowish-brown powder, m. p. 278—280°; 2-*p*-chloroanilino-, sepia crystals, decomp. about 115°; 2:5-di-*p*-chloroanilino-, pale brown crystals; 2-*o*-toluidino-, dark violet-brown crystals, m. p. 100—104°; 2:5-di-*o*-toluidino-, rust-red needles, m. p. 250—252°; 2-*m*-toluidino-, dark violet-brown crystals, m. p. 90—100° (decomp.); 2:5-di-*m*-toluidino-, crimson-red needles, m. p. 256—257°; 2-*p*-toluidino-, aggregates of violet-black needles, m. p. 134—137° (bath at 134°); 2:5-di-*p*-toluidino-, crystals, m. p. 318°; 2-*p*-acetylaminoanilino-, dark crystals; 2-*as-m*-xylydino-, reddish-brown crystals, m. p. 102°; 2:5-di-*as-m*-xylydino-, pale brown crystals, m. p. 297—300°; 2- ψ -cumidino-, brick-red crystals, m. p. 90—106°; 2:5-di- ψ -cumidino-, pale red crystals, m. p. 301—303°; 2-*o*-anisidino-, brownish-violet leaflets with metallic lustre, m. p. 114° (not sharp).

With the object of preparing monoanilides soluble in water, the aminobenzenesulphonic acids have been utilised. These do not react satisfactorily with *p*-benzoquinone, but give good results with the less reactive 2:6-dichloro-*p*-benzoquinone. By adding to a hot alcoholic solution of this a hot aqueous solution of sulphanilic acid (1 mol.), and subsequently an aqueous solution of sodium acetate (1 mol.), and then barium chloride, barium 2:6-dichloro-5-anilino-*p*-benzoquinone-*p'*-sulphonate,



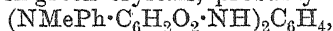
copper-red leaflets, is obtained, the mother liquor containing 2:6-dichloroquinol. If the temperature is about 60° at the beginning and about 30° at the end of the experiment, the product is mainly the barium hydrogen salt. An aqueous solution of the barium salt at 100° rapidly acquires chlorine ions and deposits a blackish-brown powder, which appears to be the barium salt of 2-chloro-5-*p*-sulphoanilino-6-hydroxy-*p*-benzoquinone. By adding sulphanilic acid to a hot aqueous solution of the first-mentioned barium salt, the barium hydrogen salt of 6-chloro-2:5-dianilino-*p*-benzoquinone-*p'**p''*-disulphonic acid is obtained as a brownish-black powder.

2-Methylanilino-*p*-benzoquinone, $C_6H_3O_2 \cdot NMePh$, prepared by adding a cold 50% acetic acid solution of methylaniline (1 mol.) to an aqueous solution of *p*-benzoquinone (2 mols.), forms dark red

needles, m. p. 125—130°. 2:5-Dimethylanilino-*p*-benzoquinone, leaflets, m. p. 205°, is obtained from its components in alcoholic solution.

2-Methylanilino-*p*-benzoquinone, like all other monoanilinoquinones of the same type, yields mixed dianilinoquinones by trituration with an aromatic base or by warming with it in alcoholic solution. The following 2-methylanilino-*p*-benzoquinones of this kind have been prepared: 5-anilino-, $\text{NMePh} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NHPh}$, orange-red crystals; 5-*p*-carboxyanilino-, dark red leaflets; 5-*m*-carboxyanilino-, brownish-red crystals; 5-*m*-chloroanilino-, garnet-red needles; 5-*o*-hydroxyanilino-, brown leaflets; 5-*m*-hydroxyanilino-, brownish-yellow, metallic crystals; 5-*p*-bromoanilino-, red crystals; 5-*p*-sulphoanilino-, prepared in the presence of sodium carbonate and 3% hydrogen peroxide, and isolated as the sodium salt; 5- α -naphthylamino-, dark brown crystals; 5- β -naphthylamino-, dark violet-brown crystals; 5-*p*-benzeneazoanilino-, violet-brown crystals.

2-Methylanilino-*p*-benzoquinone (2 mols.) and *p*-phenylenediamine (1 mol.) react in boiling alcohol to form a substance, $\text{C}_{32}\text{H}_{26}\text{O}_4\text{N}_4$, brownish-green crystals, probably

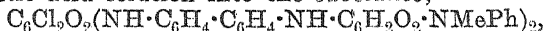


whilst in the ratio of 4:1, in alcohol, glacial acetic acid or nitrobenzene, or by moistening the mixture of the two components with a little solvent and warming on the water-bath, a dark green, crystalline substance, $[(\text{NMePh} \cdot \text{C}_6\text{H}_2\text{O}_2)_2\text{N}]_2\text{C}_6\text{H}_4$, is obtained, m. p. 250—260°.

2-Methylanilino-*p*-benzoquinone and benzidine react in warm alcohol to form the compound,

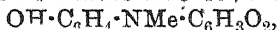


brown needles, m. p. 215—218°, which is converted by chloranil in glacial acetic acid solution into the substance,



crystals. 2-Methyl-*p*-toluidino-*p*-benzoquinone and *p*-phenylenediamine in hot alcoholic solution yield a dark green substance, probably $(\text{C}_7\text{H}_7 \cdot \text{NMe} \cdot \text{C}_6\text{H}_2\text{O}_2 \cdot \text{NH})_2\text{C}_6\text{H}_4$.

2-Ethylanilino-*p*-benzoquinone forms dark needles, m. p. 85° with previous sintering. 2-Benzylanilino-*p*-benzoquinone forms almost black needles, m. p. 60—70°, whilst 2:5-dibenzylanilino-*p*-benzoquinone, $\text{C}_8\text{H}_2\text{O}_2(\text{NPh} \cdot \text{CH}_2\text{Ph})_2$, crystallises in blood-red needles, m. p. 155—156°. 2-Methyl-*p*-toluidino-*p*-benzoquinone forms reddish-yellow needles, m. p. 127°, and 2:5-dimethyl-*p*-toluidino-*p*-benzoquinone, yellowish-brown, rhombic plates, m. p. 206°. 2-*o*-Hydroxymethylanilino-*p*-benzoquinone,

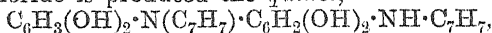


and 2:5-di-*o*-hydroxymethylanilino-*p*-benzoquinone are described.

A table is given of the colorations of the anilinoquinones in concentrated sulphuric acid. C. S.

Polymerisation Phenomena in the Simple Monoanilinoquinones. HERMANN SUIDA (*Annalen*, 1918, 416, 164—181. Compare preceding abstract).—The monoanilinoquin-

ones derived from primary bases are only stable in the pure dry state; they polymerise in solution. Dianilinoquinones, and also monoanilinoquinones derived from secondary bases, show no tendency to polymerise. The polymerisation is probably represented thus: $2C_6H_5O_2 \cdot NHAr \rightarrow C_6H_5O_2 \cdot NAr \cdot C_6H_2(OH)_2 \cdot NAr$; the dimeric meriquinonoid form produced can undergo further polymerisation. The polymerisation is brought about by heating the monoanilinoquinone at its m. p., by heating with water or dilute acetic acid, by prolonged boiling with alcohol, or by exposing its cold alcoholic solution to intense light. Thus 2-*p*-toluidino-*p*-benzoquinone yields the *dimeride*, $(C_{13}H_{11}O_2N)_2$, m. p. 265—267° (in carbon dioxide), from which by reduction with alcoholic stannous chloride is produced the *quinol*,



pale yellow crystals, m. p. 236—237° (in carbon dioxide). Dimeric *p*-toluidino-*p*-benzoquinone, $C_6H_5O_2 \cdot N(C_7H_7) \cdot C_6H_2O_2 \cdot NH \cdot C_7H_7$, produced by auto-oxidation by boiling the dimeric meriquinone in glacial acetic acid or nitrobenzene, forms violet-black crystals with green lustre, which remain unchanged at 400°; the oxidation is also effected by ferric chloride in dilute alcoholic solution.

C. S.

Anilinoquinones from Benzoquinone and the Nitroanilines. GUIDO MEYER and HERMANN SUIDA (*Annalen*, 1918, 416, 181—188).—The nitroanilines do not react as easily as aniline with benzoquinone. In cold aqueous solution, a reaction between the nitroanilines and *p*-benzoquinone is only observed when the nitroaniline is used in the form of its hydrochloride in the presence of an excess of hydrochloric acid; in all three cases, reddish-brown, crystalline additive compounds separate after some hours, but if kept in contact with the mother liquor for several weeks change into the mononitroanilino-*p*-benzoquinones. The latter are obtained immediately from the nitroanilines and *p*-benzoquinone in boiling aqueous solution. 2-*m*-Nitroanilino-*p*-benzoquinone and the *p*-nitro-compound are dark brown and do not crystallise well. The *o*-nitro-compound is less readily obtained. All three compounds have indefinite m. p.'s between 290° and 300°, and develop with sulphuric acid a reddish-violet coloration, which turns blue on warming.

In cold alcoholic solution, a reaction occurs only between *m*-nitroaniline and *p*-benzoquinone, whereby the additive compound is formed. In hot alcoholic or, better, hot glacial acetic acid solution, the 2:5-dinitroanilino-*p*-benzoquinones, decomp. 310—360°, are obtained.

The nitroanilino- and dinitroanilino-*p*-benzoquinones are not attacked by mild reducing agents. Tin and hydrochloric acid convert the latter into phenylenediamines and aminoanilinoquinols, which could not be isolated. *p*-Nitroanilino-*p*-benzoquinone was reduced by tin and hydrochloric acid to a base, which was isolated as the *sulphate*, $C_6H_3(OH)_2 \cdot NH \cdot C_6H_4 \cdot NH_2 \cdot 2H_2SO_4$, *prismatic needles; the base itself could not be isolated.

C. S.

Action of the Isomeric Chloromethylanilines on Benzo- and Tolu-quinones. HEINRICH TEUTSCHER (*Annalen*, 1918, 416, 189—202. Compare Suida and Suida, this vol., i, 79).—The chloromethylanilines in aqueous, faintly acetic acid solution yield exclusively monoanilinoquinones with *p*-benzo- and tolu-quinones; as usual, a second molecule of the quinone is reduced to the quinol. Additive products could not be isolated, although they are undoubtedly formed. In alcoholic solution, *p*-benzoquinone yields dianilinoquinones, whilst toluquinone yields only the monoanilinoquinone; here again evidence (colour change) has been obtained of the intermediate formation of additive compounds. Toluquinone, being a weaker oxidising agent than *p*-benzoquinone, reacts more slowly with the aromatic bases. Of these, *o*-chloromethylaniline reacts most slowly and the *p*-compound most rapidly.

2-*p*-Chloromethylanilino-*p*-benzoquinone, $C_6H_3O_2 \cdot NMe \cdot C_6H_4Cl$, is a dark red, crystalline powder, m. p. 145° , the *m*-chloro-compound a reddish-brown powder, m. p. 127° , sintering at 120° , and the *o*-chloro-compound crystallises in pale red needles, m. p. 133° (decomp.), sintering at 60° . 4-*p*-Chloromethylanilinotoluquinone forms a dark red, crystalline powder with metallic lustre, m. p. 156° (from aqueous solution), and dark red needles, m. p. 184° (decomp.) (from alcoholic solution), and the *o*-chloro-compound red leaflets with metallic lustre, m. p. 146° (decomp.).

2:5-Di-*p*-chloromethylanilino-*p*-benzoquinone forms deep bronze leaflets with metallic lustre, m. p. 223° , the *m*-chloro-compound, deep yellow leaflets, m. p. 198° , and the *o*-chloro-compound, reddish-bronze leaflets with metallic lustre, m. p. 258° .

2:5-Di-2':4'-dichloromethylanilino-*p*-benzoquinone, which requires the presence of hydrogen peroxide for its quick preparation, forms brick-red leaflets, m. p. 240° . C. S.

Citronellol. H. J. PRINS (*Chem. Weekblad*, 1918, 15, 1378—1380).—Distillation of citronellol yields two fractions, one with b. p. 217 — 219° and the other with b. p. 219 — 221° . The liquids probably contain isomerides, but these cannot be separated by fractionation.

When free from geraniol and other substances, but containing these isomerides, citronellol of maximum purity should have D_{10}^{20} 0.867—0.869, and its index of refraction should be n_D^{20} 1.4586—1.4589.

A. J. W.

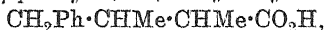
Constituents of Oil of Cassia. II. FRANCIS D. DODGE (*J. Ind. Eng. Chem.*, 1918, 10, 1005—1006. Compare A., 1916, i, 155).—Oil of cassia was found to contain cinnamaldehyde (75 to 90%), cinnamyl acetate, phenylpropyl acetate (?), *o*-methoxycinnamaldehyde, salicylaldehyde (0.1 to 0.2%), coumarin, benzoic acid, salicylic acid, an unidentified liquid acid, benzaldehyde, and *o*-methoxybenzaldehyde. [See, further, *J. Soc. Chem. Ind.*, 1919.]

W. P. S.

Constitution of Substances from Guaiacum Resin.

G. SCHROETER, L. LICHTENSTADT, and D. IRINEU (*Ber.*, 1918, 51, 1587—1613).—The milk test with extract of guaiacum resin is not entirely satisfactory, since it depends on the quality of the extract. Before examining the chemistry of the blue compound, it is necessary to determine the structure of the substance (or substances) in the resin which produces it.

The two substances of unknown constitution obtained by the dry distillation of guaiacum resin are guaiene and pyroguaiacin. The latter is known to be a hydroxymethoxy-derivative of the former (Herzig and Schiff, A., 1897, i, 254; 1898, i, 327, 530). Guaiene is now proved to be 2:3-dimethylnaphthalene by synthesis. *β*-Phenylisopropyl bromide, $\text{CH}_2\text{Ph}\cdot\text{CHMeBr}$, b. p. 107—109°/16 mm., $D_{16}^{16.4}$ 1.2908, obtained from the alcohol and hydrobromic acid (saturated at 0°) at 100°, reacts with ethyl malonate and alcoholic sodium ethoxide on the water-bath to form *ethyl β-phenylisopropylmalonate*, $\text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. 182—183°/14 mm., $D_{16}^{16.4}$ 1.0673. This is converted in the usual manner into *ethyl β-phenylisopropylmethylmalonate*, b. p. 188°/16 mm., $D_{18}^{16.4}$ 1.0505, which yields the acid, $\text{C}_{18}\text{H}_{16}\text{O}_4$, colourless crystals, m. p. 158—160° (decomp.), by hydrolysis. The acid, heated at 170—190°, yields *γ-phenyl-αβ-dimethylbutyric acid*,



b. p. 179—180.5°/13 mm., the acid *chloride* of which, b. p. 136—143°/13 mm., is converted in light petroleum (b. p. 60—70°) by aluminium chloride into 1-*keto*-2:3-dimethyl-1:2:3:4-tetrahydronaphthalene, b. p. 148—150°/17 mm., m. p. -1°, D_{21}^{21} 1.019. This is reduced by sodium and alcohol to 2:3-dimethyltetrahydronaphthol, m. p. 110—114°, b. p. 148—152°/18 mm., which loses water at above 200° and yields 2:3-dimethyl-Δ¹-dihydronaphthalene, b. p. 120—140°/16 mm., the *dibromide* of which is converted by boiling methyl-alcoholic potassium hydroxide into 2:3-dimethylnaphthalene, m. p. 104—104.5° (picrate, m. p. 123—124°), which is identical with guaiene.

Pyroguaiacin is converted by boiling alcoholic potassium hydroxide and methyl sulphate into *pyroguaiacin methyl ether*, $\text{C}_{19}\text{H}_{10}(\text{OMe})_2$, leaflets, m. p. 149—150°, the oxidation of which by sodium dichromate and glacial acetic acid at 95—115° yields *pyroguaiacinquinone methyl ether*, $\text{C}_{14}\text{H}_{14}\text{O}_4$, yellow needles, m. p. 241—242°. For reasons given below, pyroguaiacin is almost certainly 6-hydroxy-7-methoxy-2:3-dimethylnaphthalene.

Guaiaretic acid, the extraction of which from guaiacum resin by ether is described in detail, has the formula $\text{C}_{20}\text{H}_{14}\text{O}_4$ (Herzig and Schiff, *loc. cit.*, give $\text{C}_{20}\text{H}_{12}\text{O}_4$), and is now found to be optically active, $[\alpha]_D^{20}$ -94° in alcohol, and unsaturated. It is converted by methyl sulphate and hot aqueous-alcoholic potassium hydroxide into a *methyl ether*, $\text{C}_{18}\text{H}_{16}(\text{OMe})_2$, colourless needles, m. p. 94—95°, $[\alpha]_D^{20}$ -92° in alcohol, which is reduced by sodium and boiling alcohol or in solution in tetrahydronaphthalene at 180° by hydrogen and a nickel catalyst under a pressure of 40—50 kilog.

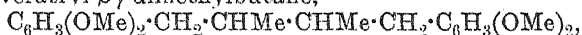
to *hydroguaiaretic acid methyl ether*, $C_{18}H_{18}(OMe)_4$; in both cases a mixture of the *i*-acid, crystals, m. p. 100—101°, and the *l*-acid, flat prisms, m. p. 86—87°, $[\alpha]_D -27^\circ$ in alcohol, is obtained.

Herzig and Schiff's *norguaiaretic acid* (*loc. cit.*), obtained in poor yield from guaiaretic acid and boiling hydriodic acid, is obtained in much better yield from hydroguaiaretic acid methyl ether, and is reconverted into this by methylation; it is therefore *norhydroguaiaretic acid*.

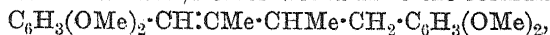
i-Dibromohydroguaiaretic acid methyl ether, $C_{18}H_{16}Br_2(OMe)_4$, colourless needles, m. p. 130·5—131·5°, is obtained by the bromination of *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid, dehydroguaiaretic acid methyl ether (below) being also formed in the latter case. *l*-Dibromohydroguaiaretic acid methyl ether, colourless crystals, m. p. 121—122°, $[\alpha]_D -42^\circ$ in alcohol, is obtained by brominating *l*-hydroguaiaretic acid methyl ether.

i-Dinitrohydroguaiaretic acid methyl ether, $C_{18}H_{16}(NO_2)_2(OMe)_4$, yellow crystals, m. p. 150—151°, obtained by adding nitric acid, D 1·4, to *i*-hydroguaiaretic acid methyl ether or guaiaretic acid methyl ether in glacial acetic acid solution, is smoothly reduced in tetrahydronaphthalene solution by hydrogen and nickel to *i*-diaminohydroguaiaretic acid methyl ether, faintly violet needles, m. p. 124—125°; attempts to resolve this base by means of *d*-tartaric acid were unsuccessful. *l*-Dinitrohydroguaiaretic acid methyl ether, yellow crystals, m. p. 122—123°, $[\alpha]_D -49·5^\circ$ in glacial acetic acid, is obtained by the nitration of *l*-hydroguaiaretic acid methyl ether.

The reduction of *l*-guaiaretic acid and of its methyl ether yields a mixture of optically active and inactive hydro-derivatives, and therefore possibly racemisation has occurred. Since it is shown, however, that the hydro-derivatives racemise with great difficulty, an alternative explanation of the formation of the inactive modification is that a second carbon atom is rendered asymmetric by the reduction, the inactive hydro-derivative being internally compensated. In favour of the symmetric structure thus postulated is the formation of the probably symmetrically substituted dibromo- and dinitro-derivatives and the failure to resolve the diamino-derivative. Hydroguaiaretic acid methyl ether would therefore be $\alpha\beta$ -diveratryl- $\beta\gamma$ -dimethylbutane,



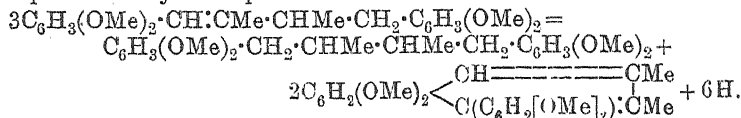
and guaiaretic acid methyl ether would have the formula



the positions of the two methyl groups being determined by the fact that guaiaretic acid can be converted through pyroguaiacin into guaiene (2:3-dimethylnaphthalene).

An extraordinary transformation of guaiaretic acid methyl ether is its *reduction* to hydroguaiaretic acid methyl ether by potassium permanganate in acetone-glacial acetic acid solution, veratric acid also being formed. The explanation is found in the action of Hübl's iodine solution on guaiaretic acid methyl ether (1 mol.),

whereby a mixture of *i*-hydroguaiaietic acid methyl ether and *dehydroguaiaietic acid methyl ether*, $C_{22}H_{24}O_4$, colourless crystals, m. p. 178·5—179°, optically inactive, is obtained in the proportion of 1:2 by the consumption of 1 mol. of iodine. This change is represented by the equation



It is probable, therefore, that in the preceding reaction with potassium permanganate, a portion of the guaiaietic acid methyl ether undergoes ring closure to a naphthalene derivative (which is then oxidised, yielding veratric acid and other products), the hydrogen produced reducing another portion to hydroguaiaietic acid methyl ether, which is stable towards permanganate.

By treatment with 2*N*-sodium hydroxide and methyl sulphate, guaiaconic acid yields a *methyl ether*, an amorphous, yellow powder, m. p. 94—102°, softening at 82°, which, unlike guaiaconic acid, does not develop a blue colour with lead peroxide. By oxidation with potassium permanganate in acetone-glacial acetic acid solution, the ether yields a comparatively large amount of veratric acid and other products, which were not identified.

Believing at first that guaiane was 1:2-dimethylnaphthalene, the authors synthesised this substance as follows. By treatment of their sodio-derivatives with methyl iodide in warm benzene, the β -phenylethylmalonic esters yield, respectively, *methyl β -phenylethylmethylmalonate*, b. p. 178—180°/18 mm., and the *ethyl ester*, b. p. 182—184°/12 mm., from which *β -phenylethylmethylmalonic acid*, colourless crystals, m. p. 150° (decomp.), is obtained. At 150—180°, the acid is converted into *γ -phenyl- α -methylbutyric acid*, b. p. 167°/11 mm., the acid chloride of which, b. p. 125°/12 mm., is converted in light petroleum solution by aluminium chloride into 1-*keto-2-methyl-1:2:3:4-tetrahydronaphthalene*, b. p. 127—131°/12 mm. This is converted by ethereal magnesium methyl iodide into 1-*hydroxy-1:2-dimethyl-1:2:3:4-tetrahydronaphthalene*, b. p. 135—140°/15 mm., m. p. 64—66°, which at 160—180° yields 1:2-*dimethyl- Δ^1 -dihydronaphthalene*, b. p. 250—251°/atm. or 114—116°/15 mm., D^{17}_D 0·9885, n_D 1·5763. The *dibromide* of the latter, a pale yellow oil, is converted by boiling methyl-alcobolic potassium hydroxide into 2-*methyl-1-methylene- Δ^2 -dihydronaphthalene*, b. p. 157°/15 mm., which yields 1:2-*dimethylnaphthalene*, b. p. 139—140°/15 mm. (*micrate*, orange-red crystals, m. p. 129·5—130·5°), by boiling with glacial acetic acid containing hydrogen chloride.

C. S.

Classification of Organic Colouring Matters. M. DOMINIKIEWICZ (*Chem. Zeit.*, 1918, **42**, 549—550, 562—564).—In the method of classification proposed, the substances are arranged under chief types depending on the constitution of the

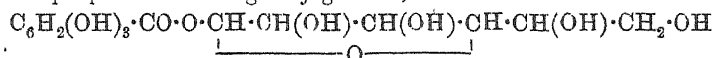
nucleus, these types being subdivided into classes. The types include the quinone type, the diphenylmethane type, the safranine type, the indigo type, etc. Sulphur derivatives and substances of unknown constitution form two separate classes. W. P. S.

Tannin and the Synthesis of Similar Substances. V.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, **51**, 1760—1804. Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437).—Previous attempts to prepare pentadigalloylglucose did not lead to the desired result, owing to the unfavourable properties of the methylcarbonato-compounds. Recently, however, it has been found possible to prepare the penta-acetyl derivatives of *m*- and *p*-digallic acids and the corresponding chlorides in the crystalline state (A., 1918, i, 172); from these, the penta-(penta-acetyldigalloyl)-glucoses have now been prepared, as well as the corresponding penta-(digalloyl)-glucoses. Penta-(*m*-digalloyl)- β -glucose is shown to be remarkably similar to Chinese tannin, the only point of difference noted being in the specific rotation in aqueous solution. Since, however, the solutions are colloidal in character and their optical activity is greatly influenced by small factors, the authors do not consider the discrepancy is necessarily fundamental.

The chemistry of the pentagalloylglucoses has been further studied (compare A., 1915, i, 437), and, through the triacetyl-galloyl derivatives, it has now been found possible to isolate products which consist almost entirely of the pentagalloyl derivatives of α - and β -glucose respectively.

The preparation of 1-galloylglucose,



is also described, this being the first acyl derivative of glucose to which a definite structure can be with certainty assigned. It is in all respects identical with the glucogallin isolated by Gilson from Chinese rhubarb (A., 1903, i, 355).

Penta-acetyl-m-digalloyl chloride, $\text{C}_6\text{H}_2(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OAc})_2 \cdot \text{COCl}$, six-sided plates, m. p. 180° (corr.), after slight previous softening, is obtained by the action of phosphorus pentachloride on *m*-digallic acid in the presence of chloroform, and is converted by methyl alcohol in the presence of quinoline into methyl penta-acetyl-*m*-digallate, m. p. 167—168° (corr.) (compare A., 1918, i, 174). It reacts with β -glucose to yield *penta-(penta-acetyl-m-digalloyl)- β -glucose*,

$[\text{C}_6\text{H}_2(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OAc})_2 \cdot \text{CO}]_5 \text{C}_6\text{H}_7\text{O}_6$, two specimens of which had $[\alpha]_D^{18} + 3.79^\circ$ and $[\alpha]_D^{19} + 2.60^\circ$ in *s*-tetrachloroethane. [*Penta-(penta-acetyl-p-digalloyl)- β -glucose* is obtained in a similar manner; it has $[\alpha]_D^{23} + 1.54^\circ$ (in *s*-tetrachloroethane), and resembles the *m*-derivative so closely that an analytical distinction is almost impossible.] *Penta-(m-digalloyl)- β -glucose* is prepared by deacetylation of the acetyl derivative with cold aqueous sodium hydroxide at 0°, and is purified by means of the *potassium* salt; according to the method of separation, it forms

a pale brown, light, amorphous powder, or a compact, honey-yellow, brittle mass. When hydrolysed by dilute sulphuric acid, it gives approximately the same amount of dextrose and gallic acid as does Chinese tannin. When treated with diazomethane, it yields penta-(pentamethyldigalloyl)-glucose, which, like the earlier preparations, is not perfectly uniform, but which shows a very close analogy with the methyl derivative of the natural Chinese tannin. Reacetylation of penta-(*m*-digalloyl)- β -glucose shows that a certain amount of change (possibly isomerisation of the β -glucose to α -glucose derivative) occurs either during hydrolysis or on treatment with acetic anhydride.

Penta-(penta-acetyl-m-digalloyl)- α -glucose is prepared in the same manner as the β -derivative; individual preparations had $[\alpha]_D + 30.8^\circ$, $+ 27.7^\circ$, and $+ 25.5^\circ$ (in *s*-tetrachloroethane), pointing to admixture with varying amounts of the β -isomeride. [The corresponding *penta-(penta-acetyl-p-digalloyl)- α -glucose* shows the closest analogy with the β -compound.] *Penta-(m-digalloyl)- α -glucose* is a pale brown, amorphous powder which can only be distinguished from the β -glucose derivative by its specific rotation; it has $[\alpha]_D^{18} + 43.8^\circ$ (in water), $[\alpha]_D^{18} + 35.8^\circ$ (in alcohol), and $[\alpha]_D^{18} + 40.1^\circ$ (in acetone).

Acetylation of Chinese tannin yields a penta-(penta-acetyldigalloyl)-glucose closely similar to penta-(penta-acetyl-*m*-digalloyl)- β -glucose; the regenerated tannin, however, is found to differ somewhat from the original specimen.

Penta-(triacetyl-galloyl)- α -glucose, $[C_6H_2(OAc)_3 \cdot CO]_5 C_6H_7O_6$, is prepared in the usual manner from α -glucose and triacetyl-galloyl-chloride; it forms an amorphous mass, having $[\alpha]_D + 42.7^\circ$ to $+ 46.95^\circ$ in *s*-tetrachloroethane. Deacetylation is accomplished by means of sodium acetate in aqueous acetone solution; the penta-galloyl- α -glucose thus obtained is distinguished from the previous preparation (by hydrolysis of penta-[trimethylcarbonatogalloyl]- α -glucose by alkali) by a considerably higher specific rotation in aqueous and alcoholic solution, but otherwise the resemblance is very close. On treatment with acetic anhydride, the original acetyl derivative is regenerated. Diazomethane converts it into penta-(trimethylgalloyl)- α -glucose, identical with that previously described (*loc. cit.*).

Penta-(triacetyl-galloyl)- β -glucose is a pale yellow, amorphous mass which has $[\alpha]_D^{20} + 5.61^\circ$ or $+ 4.1^\circ$ in *s*-tetrachloroethane; when deacetylated, it yields pentagalloyl- β -glucose, having $[\alpha]_D^{18} + 23.3^\circ$ (in alcohol), $[\alpha]_D^{18} + 13.6^\circ$ and $+ 13.1^\circ$ in 10% and 1% aqueous solution. When treated with diazomethane, it gives a penta-(trimethylgalloyl)- β -glucose which, in its properties and optical activity, closely resembles the preparation previously described (A., 1915, i, 438), but which, unlike the latter, could not be caused to crystallise. Reacetylation yields a product closely resembling the original substance. Hydrolysis of the two penta-(triacetyl-galloyl)-glucoses by alkali at 0° yields α - and β -derivatives respectively, which are quite distinct, although less so than when

sodium acetate is used. (In the case of the corresponding methyl-carbonato-compounds, practically identical products were obtained when the hydrolysis was effected by alkali at the ordinary temperature.)

Penta-(p-acetoxybenzoyl)- α -glucose, $[\text{C}_6\text{H}_4(\text{OAc})\cdot\text{CO}]_5\text{C}_6\text{H}_7\text{O}_6$, forms fine needles, m. p. 158—159° (corr.), $[\alpha]_D^{25} + 124.7^\circ$ in *s*-tetrachloroethane; during the preparation, considerable quantities of the β -isomeride are formed, which are removed during purification. The corresponding penta-(*p*-hydroxybenzoyl)- α -glucose could not be caused to crystallise, but the specific rotation of the product (+163.4° in alcohol) was considerably greater than that previously found; on reacytlation, it yielded the crystalline acetyl derivative in excellent yield. The preparation of *penta-(p-acetoxybenzoyl)- β -glucose* and of *penta-(p-hydroxybenzoyl)- β -glucose* is also described, but the substances could not be caused to crystallise, and are probably admixed with the corresponding α -derivatives.

1-Triacetylgalloyl-2:3:5:6-tetra-acetylglucose is prepared from acetobromoglucose and silver triacetyl gallate; it forms microscopic needles or four-sided leaflets, m. p. 125—126° (corr.), after slight softening, $[\alpha]_D^{25} - 24.4^\circ$ in *s*-tetrachloroethane. It may also be obtained from tetra-acetylglucose and triacetylgalloyl chloride. When dissolved in alcohol and treated with ammonia at 20°, it yields 1-monogalloyl- β -glucose, microscopic, oblique prisms or platelets, m. p. 214—215° (corr.; decomp.), when rapidly heated, 202—203° (corr.; decomp.) when slowly heated; it has $[\alpha]_D^{18} - 25.6^\circ$ in aqueous solution. The product is quite distinct from the glucogallic acid described by Feist (A., 1912, i, 566, 888; 1913, i, 70). When reacytlated, it yields triacetylgalloyltetra-acetylglucose. Its action towards enzymes has been investigated. Its identity with glucogallin is established both by chemical tests and by measurement of the crystals. *1-Galloyl- β -glucosemonoacetate* forms colourless needles, $[\alpha]_D^{18} + 10.5^\circ$ (in alcohol); it has no distinct m. p., but, when rapidly heated, is converted into a viscous, turbid liquid at about 150° after marked softening. *1-Galloyl- β -glucosetetra-acetate* (?) crystallises in needles, m. p. about 136—137°, $[\alpha]_D^{25} + 38.7^\circ$ (in alcohol), but its isolation in the pure condition is not claimed.

1-Benzoyltetra-acetylglucose is prepared from benzoyl chloride and 2:3:5:6-tetra-acetylglucose, and agrees in its properties with the product described by Zemplén and László (A., 1915, i, 651) except in specific rotation ($[\alpha]_D^{25} - 26.6^\circ$ in chloroform). *1-o-Acetoxybenzoyl-2:3:5:6-tetra-acetylglucose* crystallises in microscopic, flat prisms. It has m. p. 116—117° (corr.), $[\alpha]_D^{25} - 41.0^\circ$ in *s*-tetrachloroethane.

H. W.

Structure of β -Glucosidogallic Acid. EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, 51, 1804—1808).—The work of Fischer and Strauss (A., 1913, i, 180) has led to the supposition that β -glucosidogallic acid contains the sugar residue attached to the *p*-hydroxyl group of gallic acid; this hypothesis is confirmed by its conversion into glucosyringic acid (Mauthner, A., 1910, i, 667).

Ethyl tetra-acetylglucosidogallate is converted by diazomethane into ethyl tetra-acetylglucosyringate, from which glucosyringic acid is obtained by hydrolysis with barium hydroxide; the free acid has m. p. about 225° (decomp.) when moderately rapidly heated and $[\alpha]_D^{20} - 18.18^{\circ}$ (as sodium salt) in water.

Ethyl triacetyl-gallate has m. p. $138-139^{\circ}$ (corr.) instead of $132-134^{\circ}$ (A., 1915, i, 683).

Ethyl hexa-acetylglucosidogallate has m. p. $176-177^{\circ}$ (corr.), $[\alpha]_D^{18} - 19.0^{\circ}$ in tetrachloroethane solution. H. W.

Digitalis Substances. XXXVIII. H. KILIANI (*Ber.*, 1918, 51, 1613—1639. Compare A., 1916, i, 493).—The preliminary crystallisation from 85% alcohol is unnecessary in order to separate the digitonin from the gintonin in "crude digitonin amylate" (*Ber.*, 1916, 49, 701). It suffices to dissolve the crude amylate in ten parts of boiling 50% alcohol; on cooling, gintonin material separates first and pure digitonin subsequently.

A sample of "soluble digitonin" supplied by Merck proved to be identical with a new glucoside obtained from the final mother liquor of the crude digitonin (*loc. cit.*).

The sugar syrup previously obtained (*loc. cit.*) could not be made to crystallise, because the sugars in the syrup, which had been produced in an alcoholic medium, are present chiefly in the form of ethyl glucosides. After a second hydrolysis with hydrochloric acid, a partial crystallisation can be effected, and *d*-galactose obtained by inoculation; dextrose, identified as *d*-gluconic acid, is present, and apparently also a third sugar, a ketose, since the syrup is shown to contain oxalic and glycollic acids. (The hydrochloric acid was removed by silver oxide, and it is known that silver oxide acts on hexoses, particularly keto-hexoses, to produce these two acids.)

During the conversion of digitogenin, $C_{31}H_{50}O_6$, into digitogenic acid, $C_{28}H_{44}O_8$, three atoms of carbon are removed. Their fate has not been ascertained; it is shown that they do not appear as acetone, acetaldehyde, malonic, propionic, or carbonic acid.

Digitogenic acid has $[\alpha]_D - 67.1^{\circ}$ in aqueous potassium hydroxide, and forms a *magnesium* salt, $C_{28}H_{42}O_8Mg \cdot 7H_2O$, small, hard nodules of minute needles. β -Digitogenic acid has $[\alpha]_D - 60.2^{\circ}$ in aqueous potassium hydroxide, and forms a *magnesium* salt, microscopic prisms and needles with $7H_2O$. The m. p. of digitogenic acid is altered by crystallisation, and is therefore no safe criterion for identification. The acid is not reduced by hydrogen and colloidal palladium, amalgamated zinc and hydrochloric acid, or zinc dust and acetic acid.

The acid, $C_{16}H_{24}O_7$, obtained by the oxidation of digitogenic acid in about 15% yield (*loc. cit.*), is obtained in about 27% yield by oxidising the amorphous precipitate thrown down by adding water to the mother liquor of the crude digitogenic acid. It is oxidised by potassium permanganate in strongly alkaline solution,

yielding an amorphous *acid*, $C_{15}H_{22}O_7 \cdot H_2O$, decomp. $120-130^\circ$, softening at about 70° , which forms an amorphous *magnesium salt*, $(C_{15}H_{19}O_7)_2Mg_3 \cdot 5H_2O$.

The mother liquor of the crude acid, $C_{16}H_{24}O_7$ (*loc. cit.*), contains, in addition to other substances, at least two very easily soluble acids, one of which has been identified as ethylsuccinic acid.

The oxidation of gitogenic acid by hot chromic, acetic, and sulphuric acids yields an *acid*, $C_{18}H_{28}O_6$, tufts of needles, m. p. 210° , sintering at about 206° (*calcium salt*, $C_{18}H_{26}O_6Ca \cdot 2H_2O$), an *acid*, $C_{19}H_{30}O_6$, m. p. $201-202^\circ$ (*calcium salt*, $C_{19}H_{28}O_6Ca$, amorphous), and ethylsuccinic acid.

Digitoxigenin is not reduced by hydrogen and colloidal palladium, and is oxidised by chromic and acetic acids, yielding a neutral *substance*, $C_{19}H_{26}O_4$, crystals, m. p. 185° .

Digitaligenin forms an *acetyl derivative*, $C_{22}H_{28}O_3Ac_2$, colourless prisms or needles, m. p. $201-202^\circ$ (digitaligenin also has m. p. $201-202^\circ$, not $210-212^\circ$, as stated previously), and is reduced in aqueous methyl-alcoholic solution by hydrogen and colloidal palladium, yielding a *substance*, $C_{19}H_{28} \text{ (or } 30) O_3 \cdot H_2O$, crystals, m. p. $182-184^\circ$, sintering at 175° , which is oxidised by chromic and acetic acids, yielding a neutral *substance*, $C_{19}H_{26} \text{ (or } 28) O_3$, stout crystals, m. p. $190-192^\circ$, and an *acid*, $C_{14}H_{20}O_4$ (by analysis) or $C_{11}H_{16}O_3$ (by titration and by analysis of the *calcium salt*), colourless prisms sintering at $240-245^\circ$ without melting. C. S.

The Isomeric Lactones, Caryophyllin and Urson.

FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1918, **40**, 1917—1939).—Comparison of caryophyllin and urson shows a very close similarity of these compounds; in strictly chemical properties no differences have been observed, but the variations in the physical properties appear to warrant the conclusion that they are isomerides of very similar structure. The balance of evidence is in favour of a lactonic constitution, but in certain respects (practically instantaneous neutralisation of alkali in alcoholic solution, opening of lactone ring on acetylation) an unusual behaviour is exhibited.

Caryophyllin is most readily obtained in the pure state through the potassium salt, and crystallises in white needles ($+2H_2O$); the anhydrous substance has m. p. about 310° (corr.), $[\alpha]_D^{25} + 54.5^\circ$ in alcoholic solution; in a vacuum tube at $280-300^\circ$ it sublimes in characteristic rosettes. The *potassium salt* forms well-defined prisms ($+1.5H_2O$); the anhydrous salt has $[\alpha]_D^{25} + 63.4^\circ$ in ethyl alcohol, $[\alpha]_D^{24.5} + 67.7^\circ$ in methyl alcohol. Analyses lead to the formula $C_{30}H_{40}O_4K$ for the salt, and hence to $(C_{10}H_{16}O)_3$ for caryophyllin. The *calcium, lead, magnesium, zinc, and silver salts* are described.

Acetylation of caryophyllin under various conditions leads to the formation of *diacetylcaryophyllinic acid* and acetylcaryophyllin; the former substance is somewhat unstable, but can be obtained in the pure state by evaporation of an ethereal solution of the crude acetylation product at the ordinary temperature. It slowly loses acetic acid at the ordinary temperature, and is converted into

acetylcaryophyllin by boiling ethyl alcohol or glacial acetic acid. The *potassium* salt is described. Acetylcaryophyllin forms white, efflorescent needles, m. p. 260—265°, and yields a *potassium* salt which is readily soluble in alcohol. A very sparingly soluble substance, possibly a polymeric acetate, is also obtained during the acetylation of caryophyllin.

Oxidation of caryophyllin with fuming nitric acid yields caryophyllic acid, which is shown to be a somewhat unstable, tribasic acid, $C_{27}H_{45}O_3(CO_2H)_3$, giving a characteristic, sparingly soluble, mono-*potassium* salt. When heated with acetic anhydride it yields a compound, m. p. 210—213° (slight decomp.), which appears to be an acetyl dilactone, $C_{31}H_{46}O_6$, a molecule of carbon dioxide being eliminated during the process.

Urson in its general properties is very similar to caryophyllin. The most striking difference is shown by the potassium salts, that derived from urson being freely soluble in ethyl alcohol, in which the caryophyllin salt is sparingly soluble; a method of separation is based on this dissimilarity. The *lead*, *zinc*, *magnesium*, and *ammonium* (?) salts of urson are described. Urson diacetate (diacetylursonic acid) closely resembles the corresponding derivative of caryophyllin, but is, in general, more soluble and less stable. Decomposition to the mono-acetate occurs so readily that it was found impossible to prepare a pure compound. Acetylurson separates from alcohol in plates or prisms (+ 5H₂O) quite different in appearance from the caryophyllin compound. It was not found possible to purify the product formed by the oxidation of urson with fuming nitric acid.

H. W.

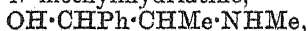
4-Phenylcoumarins. II. ADOLF SONN (*Ber.*, 1918, 51, 1829—1832. Compare A., 1918, i, 401).—Further examples of the formation of 4-phenylcoumarins are given.

Chloroacetylresorcinol dimethyl ether, m. p. 114—115° after softening at 112° [Tambor and du Bois (*A.*, 1918, i, 395) give 119°], is obtained by the action of hydrogen chloride on an ethereal solution of resorcinol dimethyl ether and chloroacetonitrile in the presence of zinc chloride, and is converted by potassium cyanide into *cyanoacetylresorcinol dimethyl ether*, prisms or plates, m. p. 152—153°. The latter condenses with phloroglucinol in glacial acetic acid solution under the influence of zinc chloride and hydrogen chloride, yielding 5:7-*dihydroxy-2':4':4'-dimethoxy-4-phenylcoumarin*, hexagonal prisms, m. p. 232° (decomp.).

Similarly, *cyanoacetylcatechol*, m. p. 222° (decomp.), after previous softening, condenses with phloroglucinol to 3':4':5:7-*tetrahydroxy-4-phenylcoumarin*, which, after being purified through the acetyl derivative, forms platelets (+ 2H₂O), m. p. about 270° (decomp.).

H. W.

Improvements in and Relating to Synthetic Drugs [Mydriatic Alkaloids]. NAGAYOSHI NAGAI (*Brit. Pat.* 120936).—Synthetic racemic *N*-methylmydriatine,



or its salts is prepared by the condensation of benzaldehyde with nitroethane by agitation for several hours at the ordinary temperature in the presence of a small quantity of a solution of a weak alkali, such as an alkali carbonate or hydrogen carbonate, or phosphate, or pyridine, etc. The condensation product, phenylnitropropanol, $\text{OH}\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{NO}_2$, is separated by extraction with ether and freed from benzaldehyde by shaking the ethereal solution with aqueous sodium hydrogen sulphite. The oily residue is dissolved in dilute alcohol, the calculated quantity of formaldehyde is added, and the mixture is reduced at a low temperature by adding dilute acetic acid and zinc dust. The liquid is filtered and the zinc precipitated by hydrogen sulphide; the solution is evaporated in a vacuum and the resinous residue is shaken with dilute hydrochloric acid and ether. The hydrochloride of the base is obtained by evaporating the aqueous layer, and is recrystallised from absolute alcohol. This synthetic ephedrine differs in constitution from Fournau's ephedrine (A., 1907, i, 762), and is the racemic form of natural ephedrine.

J. F. B.

Alkaloids of the Betel Nut. KARL FREUDENBERG (*Ber.*, 1918, 51, 1668—1682).—Guvacine is 1:2:5:6-tetrahydropyridine-3-carboxylic acid according to the author (A., 1918, i, 403) and 1:2:5:6-tetrahydropyridine-4-carboxylic acid according to Hess and Leibbrandt (A., 1918, i, 401). The author now shows that his view is the correct one by (i) the direct comparison (mixed m. p.'s, etc.) of corresponding derivatives of guvacine and Wohl and Johnson's 1:2:5:6-tetrahydropyridine-3-carboxylic acid, (2) by the identity of *N*-methylguvacine with natural arecaidine, and (3) by a comparison of dihydroguvacine with nipecotinic acid and *isonipecotinic* acid. Contrary to the statement of Hess and Leibbrandt, dihydroguvacine differs in every way from *isonipecotinic* acid, and is completely identical with nipecotinic acid (piperidine-3-carboxylic acid). Dihydroguvacine has m. p. 261° (decomp.; corr.), not above 320° , as stated by Hess and Leibbrandt (*loc. cit.*). The nipecotinic acid used by Hess and Leibbrandt was in reality almost pure *isonipecotinic* acid. Several other errors in their paper are corrected; for example, *N*-methylguvacine (arecaidine, arecaine), when esterified by alcoholic hydrogen chloride, is not demethylated at the nitrogen atom.

C. S.

The Physical Constants of Nicotine. I. Specific Rotatory Power of Nicotine in Aqueous Solution. HARRY JEPHCOTT (T., 1919, 115, 104—108).

Some Derivatives of Pyrrole. IV. G. KARL ALMSTRÖM (*Annalen*, 1918, 416, 279—290. Compare A., 1913, i, 1240; 1915, i, 989; 1916, i, 568).—In some reactions 5-hydroxy-4-acetyl-1:3-diphenylpyrrole (A., 1916, i, 568) behaves as though it were the 5-keto-compound. It is not attacked by boiling alkali hydroxide and benzaldehyde, but by heating with methyl iodide and alcoholic sodium methoxide at 100° yields a mixture of 4-acetyl-1:3-diphenyl-4-

methyl-5-pyrrolone, colourless crystals, m. p. 115—116° (*semicarbazone*, m. p. 217° [decomp.]), and 1:3-diphenyl-4-methyl-5-pyrrolone, colourless needles, m. p. 113—114°. The latter of these is also obtained by heating the former with moderately concentrated sulphuric acid, and is oxidised by chromic and acetic acids to *phenylmethylmaleinphenylimide*, $\begin{matrix} \text{CMe}\cdot\text{CO} \\ | \\ \text{CPh}\cdot\text{CO} \end{matrix} > \text{NPh}$, pale yellow, quadratic plates, m. p. 106—107°, from which aniline and *phenylmethylmaleic anhydride*, m. p. 94—95°, are obtained by boiling with alcoholic sodium ethoxide.

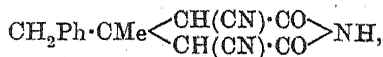
By heating on the water-bath with 2*N*-sodium hydroxide and a large excess of methyl sulphate, 5-hydroxy-4-acetyl-1:3-diphenylpyrrole yields 1:3-diphenyl-4-methyl-5-pyrrolone and 4-acetyl-5-methoxy-1:3-diphenylpyrrole, colourless crystals, m. p. 101°, which forms a *semicarbazone*, pale yellow crystals, m. p. 215° (decomp.), yields 1:3-diphenyl-5-pyrrolone by heating with moderately concentrated sulphuric acid, and is converted into 4-cinnamoyl-5-methoxy-1:3-diphenylpyrrole, yellow crystals, m. p. 111—112°, by heating with aqueous-alcoholic sodium hydroxide and benzaldehyde.

1:3-Diphenyl-4-ethyl-5-pyrrolone, colourless plates, m. p. 118—119°, yields *phenylethylmaleinphenylimide*, yellow, rhombic plates, m. p. 79—80°, by oxidation, from which aniline and *phenylethylmaleic anhydride*, m. p. 46°, are obtained by the action of sodium ethoxide.

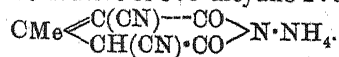
5-Hydroxy-4-acetyl-1:3-diphenylpyrrole does not yield crystalline products by treatment with acetic anhydride, diazomethane, or acetyl chloride, but it reacts with magnesium methyl iodide and then with acetyl chloride to form a substance, $\text{C}_{18}\text{H}_{15}\text{O}_3\text{N}$, colourless needles, m. p. 119—120°. C. S.

General Reaction of Ketones. I. GUARESCHI (*Gazzetta*, 1918, 48, ii, 83—98).—The author has extended his work on the condensation of ketones with ethyl cyanoacetate in presence of ammonia or an amine (A., 1902, i, 819) to benzyl methyl ketone and its homologues in order to ascertain which ketones react incompletely or not at all with the cyanoacetate, and to study the manner in which the new compounds decompose with formation of hydrocarbons.

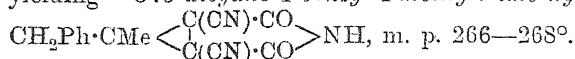
3:5-Dicyano-2:6-diketo-4-benzyl-4-methylpiperidine,



the 1-ammonium derivative of which is formed from benzyl methyl ketone, ethyl cyanoacetate, and ammonia, crystallises in shining needles or prisms, m. p. 255—257°, and has an acid reaction in aqueous solution; its *ammonium* salt is crystalline, and in aqueous solution decomposes with difficulty into toluene and the ammonium derivative of 3:5-dicyano-2:6-diketo-4-methyl- Δ^3 -tetrahydropyridine,

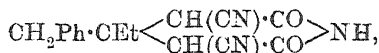


With bromine water 3:5-dicyano-2:6-diketo-4-benzyl-4-methylpiperidine gives a dibromo-derivative, which, when boiled with alcohol, best with addition of a little formic acid, rapidly loses bromine, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,

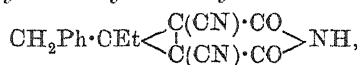


β -Phenylethyl methyl ketone yields 3:5-dicyano-2:6-diketo-4- β -phenylethyl-4-methylpiperidine, which has been already described.

3:5-Dicyano-2:6-diketo-4-benzyl-4-ethylpiperidine,

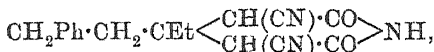


obtained from benzyl ethyl ketone, forms crystals, m. p. 222—226°, which absorb bromine, giving the dibromo-derivative. The latter loses its bromine when boiled with alcohol and formic acid, yielding 3:5-dicyano-4-benzyl-4-methyltrimethylenedicarbonimide,



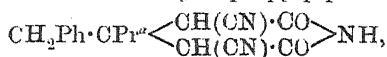
m. p. 226—228°.

3:5-Dicyano-2:6-diketo-4- β -phenylethyl-4-ethylpiperidine,



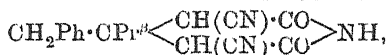
prepared from β -phenylethyl ethyl ketone, forms crystals, m. p. 181—183°.

3:5-Dicyano-2:6-diketo-4-benzyl-4-propylpiperidine,



forms white crystals, m. p. 225°.

3:5-Dicyano-2:6-diketo-4-benzyl-4-isopropylpiperidine,



forms colourless needles, m. p. 248·5—249·5°. When treated with alcohol and formic acid, its dibromo-derivative decomposes, yielding a colourless, crystalline compound, m. p. 255—257°, which is probably 3:5-dicyano-4-benzyl-4-isopropyltrimethylenedicarbonimide.

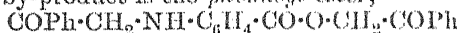
Benzyl isobutyl ketone condenses with ethyl cyanoacetate and ammonia, giving a small quantity of a compound which crystallises in needles, m. p. 223—225°, but was not analysed.

With sodium hydrogen sulphite, benzyl methyl ketone, β -phenylethyl methyl ketone, and benzyl ethyl ketone form crystalline compounds, but this is apparently not the case with β -phenylethyl ethyl ketone or benzyl isobutyl ketone.

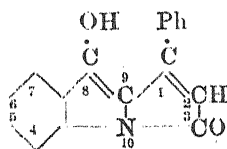
T. H. P.

The Three Phenacylaminobenzoic Acids. M. SCHOLTZ (*Ber.*, 1918, 51, 1645—1653).—The three aminobenzoic acids react with α -bromoacetophenone in boiling alcohol to form α -phenacylaminobenzoic acid, $\text{COPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, yellow leaflets, m. p. 190° (*phenylhydrazone*, yellow needles, m. p. 156°), the *m*-isomeride,

colourless crystals, m. p. 202°, and the *prismoride*, colourless needles, m. p. 211° respectively. If alkali hydroxide or carbonate also is present in the reaction in the case of the ortho- and para-compounds, a by-product is the *phenacyl ester*,

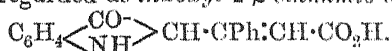


(*o*-ester, hair-like crystals, m. p. 180°; *p*-ester, colourless needles, m. p. 186°). By treatment with boiling acetic anhydride *m*- and *p*-phenacylaminobenzoic acids are converted into the corresponding *N*-acetyl derivatives, pointed prisms, m. p. 217°, and leaflets, m. p. 176°, respectively, but the ortho-compound is converted into a *sub-*



stance, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 288°, which is regarded as 8-hydroxy-3-keto-1-phenylpropenyl-2:1-indole (annexed formula). It develops a blood-red coloration with alcoholic ferric chloride, forms a *dibromide*, $\text{C}_{17}\text{H}_{11}\text{O}_2\text{NBr}_2$, pale yellow needles, m. p. 265°, and is converted by hot aqueous

alcoholic potassium hydroxide into the *potassium salt of an acid*, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}$, colourless needles, m. p. 300° (decomp.), which does not give a coloration with ferric chloride, forms a *dibromide*, pale yellow needles, and yields a *phenylhydrazone*, yellow needles, m. p. 221°, and is therefore regarded as *indoxyl-2-β-cinnamic acid*,



It is acetylated by warming with acetic anhydride, but the *product*, $\text{C}_{17}\text{H}_{13}\text{O}_3\text{N}\cdot\text{Ac}$, rhombic crystals, m. p. 167°, no longer exhibits the properties of an acid; it regenerates indoxylcinnamic acid after prolonged boiling with aqueous sodium hydroxide.

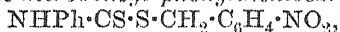
By boiling with phenylhydrazine in glacial acetic acid all three phenacylaminobenzoic acids yield the *phenylhydrazone* of *s*-phenacylphenylhydrazine, $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{NHPh}$, yellow needles, m. p. 147° (*acetyl derivative*, $\text{C}_{20}\text{H}_{19}\text{N}_4\text{Ac}$, yellow crystals, m. p. 201°).

o-Bromoacetophenone and phenylhydrazine react in boiling alcohol to form, not the preceding compound, but a *substance*, $\text{C}_{25}\text{H}_{24}\text{N}_4$, colourless needles, m. p. 174°, which is regarded as *tetra-phenyl-β-tetracarbazone*, $\text{CPh}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{N}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CPh}$, and is isomeric with the substance, m. p. 137°, obtained by Hess in 1886 from the same two reagents in alcoholic solution at 0°. C. S.

Aldehyde Derivatives of Rhodanines and their Fission Products. I. RUDOLF ANDREASCH (*Monatsh.*, 1918, 39, 419--440).—A study of the oxidation, reduction, and fission of various condensation products of aldehydes and rhodanines.

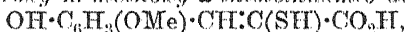
A solution of phenylbenzylidenetherhodanine in boiling glacial acetic acid is oxidised by bromine to phenylbenzylidenethiocarbimideglycolide, m. p. 209° (compare A., 1917, i, 663, in which the m. p. is given as 239° in error); similarly, phenyl-*o*-nitrobenzylidenetherhodanine yields *phenyl-*o*-nitrobenzylidenethiocarbimideglycolide*, woolly needles, m. p. 204°.

The following substances have been prepared with a view to the study of their reduction: 5-ethylrhodanine (from ethyl α -bromobutyrate and ammonium dithiocarbamate), yellowish-white, crystalline powder, m. p. 105°; 3-phenyl-5-ethylidenerhodanine, thin, pale yellow plates, m. p. 123°; 3-phenyl-5-ethylrhodanine, pale yellow needles, m. p. 83°; *o*-nitrobenzyl phenyldithiocarbamate,

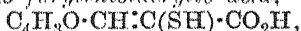


sulphur-yellow needles, m. p. 120—121°. Attempts to reduce ethylidenerhodanine and phenylethylidenerhodanine have not yielded satisfactory results up to the present.

The various aldehyde condensation products of the rhodanines are found to be decomposed with widely differing velocities by alkali; those containing a hydroxy-group in the phenyl residue are particularly resistant, so that, in general, they are only decomposed under conditions which lead to the further degradation of their fission products. The most suitable reagent is a solution of sodium amyl-oxide in amyl alcohol, probably by reason of the higher temperature which can be attained. Under these conditions, phenylpiperonylidenerhodanine yields phenylthiocarbimide and *methylenedioxy- α -thiolcinnamic acid*, $\text{CH}_2\text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH} : \text{C}(\text{SH}) \cdot \text{CO}_2\text{H}$, yellow, microscopic needles, which begin to decompose at ca. 170° and are completely molten at 208—210°. The latter acid is transformed by iodine into *disulphidobismethylenedioxy-cinnamic acid*, m. p. 228°. Similarly, *p*-hydroxy-*m*-methoxy- α -thiolcinnamic acid,



pale chrome-yellow, rhombic plates, m. p. 183° after softening at 170°, is obtained from the condensation product of vanillin and phenylrhodanine, whilst the anhydride of *o*-hydroxy- α -thiolcinnamic acid (m. p. of benzyl derivative, 164—165°) is prepared from phenyl-*o*-hydroxybenzylidenethiocarbimideglycolide. Phenylfurylidenerhodanine yields *furylthiolacrylic acid*,



fine needles, m. p. 102—103°, which is transformed by iodine into the corresponding *disulphido-acid*, lemon-yellow needles or hexagonal plates, m. p. 190—191°. Fission of *p*-hydroxybenzylidenerhodanine, m. p. 274° after softening at 260°, did not lead to the isolation of *p*-hydroxy- α -thiolcinnamic acid, but its formation was proved by the separation of its *benzyl* derivative, colourless, microscopic needles, m. p. 183°. The free *acid*, chrome-yellow needles, m. p. 186°, was prepared by the action of a solution of sodium amyl oxide in hot amyl alcohol on *phenyl-p*-hydroxybenzylidenerhodanine, cadmium-yellow needles, m. p. 285°. The corresponding *disulphido-acid* is a yellow, crystalline powder, m. p. 197°. *p*-Dimethylamino- α -thiolcinnamic acid has m. p. 160°; the corresponding *disulphido-acid* is a scarlet powder, m. p. 198°.

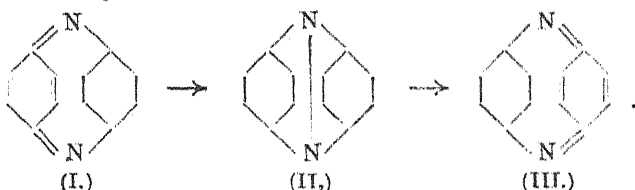
p-Aminobenzylidenerhodanine forms fine, woolly needles resembling chromium trioxide which soften at about 200°, and are not completely melted at 290°; 2:4-diketo-5-*p*-aminobenzylidenethiazol-

idine, $\begin{array}{c} \text{CO} - \text{S} \\ | \quad \diagup \\ \text{NH} \cdot \text{CO} \end{array} > \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, is a dark reddish-brown powder

which further darkens from about 200° , and has no definite m. p. Attempts to decompose these substances, as also phenyl *o*-nitrobenzyl idenerhodanine, by alkali led to negative results. H. W.

Parabanic Acid. ROBERT BEHREND and ADOLF ASCHÉ (*Annalen*, 1918, **416**, 226—228).—Parabanic acid can be obtained in about 33% yield by rapidly adding 8.4 grams of uric acid to 39 c.c. of nitric acid, D 1.3, heated at 70° , evaporating the solution to dryness, and evaporating the residue two or three times with nitric acid, D 1.4, until the evolution of gas ceases. The product is crystallised from boiling water. C. S.

New Compounds to be employed as Colouring Matters or in the Production of Colouring Matters. ANDREA ANGEL (Eng. Pat., 121347, 1917).—A new type of compounds, for which the name of "parazenes" is suggested, contains two benzene nuclei (or nuclei of benzene derivatives or other cyclic groups) linked together through four para-carbon atoms of the nuclei by two nitrogen atoms. Of the three phases of the formula which may be assigned to parazene, two (I and III) become identical in the absence of unsymmetrical substitution:



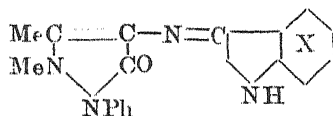
Parazenes are prepared by heating a parahalogen substituted aniline or α -naphthylamine, or derivatives of either containing indifferent groups in the nuclei, with a condensing agent, such as zinc chloride, ferric chloride, aluminium chloride, or phosphoric oxide. The product of the reaction is a hydroxyparazene, which is converted by reduction into parazene. The parazene thus obtained from *p*-chloroaniline is a dark blue powder which, when dissolved in dilute acetic acid, may be used for dyeing wool or silk. Special colouring matters may be produced by introducing auxochromic groups by the ordinary methods. Parazenes will form salts with acids by addition to one or both of the nitrogen atoms. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] C. A. M.

Interaction of Aliphatic Diazo-compounds and Diphenylketen. J. SUREDA Y BLANES (*Anal. Fis. Quim.*, 1918, **16**, 611—624).—With phenyldiazomethane, diphenylketen produces a substance, $\text{C}_{21}\text{H}_{16}\text{ON}_2$, white crystals, m. p. 196° . Diphenyldiazomethane and diphenylketen yield yellow crystals, m. p. 133 — 135° (decomp.). The product from diphenylenediazomethane and diphenylketen is a dark yellow powder, m. p. 157° (decomp.). The constitution of these substances is being further investigated. A. J. W.

Preparation of True Vat Dyes from Di- and Tri-aryl-methane Dyes. HEINRICH WIELAND (D.R.-P. 308298; from *Chem. Zentr.*, 1918, ii, 782—783).—By treatment of the dyes with alkali hyposulphite solution, colourless alkali salts are obtained which are soluble in water, and are reoxidised to the original dyes with extraordinary rapidity by atmospheric oxygen. For example, crystal violet yields sodium hexamethyltri-aminotriphenyl-methanesulphonate, $C(C_6H_4 \cdot NMe_2)_3 \cdot SO_3Na$, crystallising in glistening needles.

H. W. B.

Some Derivatives of Isatin. ANDRÉ MEYER (*Compt. rend.* 1918, 167, 1070—1073).—When the amino-oxindole obtained by the reduction of isatoxime with tin and hydrochloric acid is oxidised by potassium ferricyanide in dilute solution, in addition to isatin, a small amount of a red compound is obtained. If the isatoxime is reduced by zinc and acetic acid, the zinc salt, $C_{16}H_8O_2N_2Zn$, of this red compound is obtained. From its behaviour on reduction with sodium hyposulphite or when dissolved in sulphuric acid, the author considers that the red compound is probably identical with

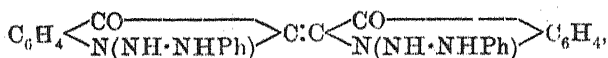


Wahl and Bagard's isindigotin.

Mixed rubazonic acids of the isatin series may be prepared by condensing, in alcoholic solution, amino-antipyrine with isatin, 5-bromoisatin, 5:7-dibromoisatin, and naphthisatin. They have the general constitution (annexed formula), where X represents the substituted benzene or naphthalene nucleus.

W. G.

Derivatives of the Indole and Indigotin Groups Substituted at the Nitrogen Atom. AUGUST ALBERT (*Annalen*, 1918, 416, 240—278. Compare A., 1916, i, 821).—1-Hydroxy-2-thio-3-benzoyloxyoxindole (A., 1915, i, 595) only reacts in the thion form in forming the acetyl derivative. In all other cases, it reacts in the thiol-form, $C_6H_4 \begin{smallmatrix} \text{CH(Obz)} \\ \text{NO} \end{smallmatrix} > C \cdot SH$. For example, it reacts with phenylhydrazine in cold alcoholic or glacial acetic acid solution to form 2-thiol-3-benzoyloxyoxindolephenylhydrazone hydrate, $NHPh \cdot NH \cdot N(OH) \begin{smallmatrix} C_6H_4 \\ C(SH) \end{smallmatrix} > CH \cdot Obz$, pale yellow plates, m. p. 123—126° (decomp.), which is also formed from the acetyl derivative, acetic acid being eliminated. The phenylhydrazone hydrate is interesting in that the sulphur can be extraordinarily easily eliminated. N/2-Sodium hydroxide converts it into 1:1'-bisphenylhydrazinoindigotin,



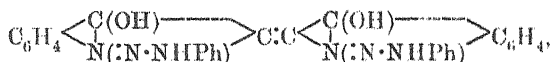
red, rectangular plates, decomp. 237—240°, darkening at 230°, in

which the presence of the two carbonyl groups is shown (1) by heating on the water-bath with aniline or *p*-toluidine and its hydrochloride, whereby the *hydrochloride* of the *anil*,



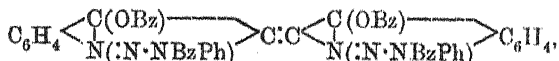
steel-blue needles, decomp. 240° , or of the *p*-*tolil*, greenish-blue crystals, decomp. 218 – 223° , is obtained, and (2) by heating with phenylhydrazine and its hydrochloride, whereby the *bisphenylhydrazone*, $\text{C}_{40}\text{H}_{34}\text{N}_{10}$, yellow plates, decomp. 200 – 206° , is obtained.

Certain reactions indicate that 1:1'-bisphenylhydrazinoindigotin is able to react in the tautomeric enolic form,



Thus the substance is insoluble in dilute aqueous sodium hydroxide, and is only sparingly soluble in alcohol, but dissolves extremely easily in alcoholic sodium hydroxide, the colour of the solution changing from yellow to blood-red; the yellow colour is regenerated by the addition of water. These colour changes are still more pronounced in the case of the 1:1'-bisphenylmethylhydrazinoindigotin mentioned below; the yellow colour of its alcoholic solution is changed to dark green by alcoholic potassium hydroxide, and is regenerated by the addition of water. The presence of two hydroxyl groups is proved by means of benzoyl chloride. 1:1'-Bisphenylhydrazinoindigotin is boiled with 10*N*. sodium hydroxide until the dark red *sodium* derivative is formed, the mixture is then cooled and treated with benzoyl chloride, whereby, according to the conditions, the *dibenzoyl* derivative,

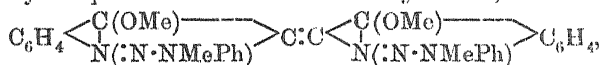
$\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}:\text{C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}_6\text{H}_4$, yellowish-red needles, m. p. 190 – 191° (this forms a *bisphenylhydrazone*, $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}(\text{:N}\cdot\text{NHPh}) \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}:\text{C} \begin{array}{c} \text{C}(\text{:N}\cdot\text{NHPh}) \\ \diagup \quad \diagdown \\ \text{N}(\text{NH}\cdot\text{NBzPh}) \end{array} \text{C}_6\text{H}_4$, pale yellow plates containing $2\text{H}_2\text{O}$, m. p. 140 – 145° [hydrated] or 186 – 189° [decomp.; anhydrous]), or the *tetrabenzoyl* derivative,



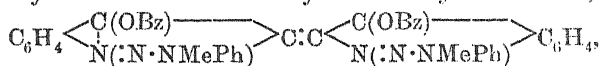
yellow or yellowish-brown, rhombic plates, m. p. 158 – 159° , is obtained. The tetrabenzoyl derivative is converted into the dibenzoyl derivative by careful treatment with sodium ethoxide, and into the bisphenylhydrazone of the latter by warming with phenylhydrazine and its hydrochloride at 50° .

By treatment with *as*-phenylmethylhydrazine, 1-hydroxy-3-benzoyloxy-2-thio-oxindole is converted into a phenylmethylhydrazone, which could not be obtained crystalline, and is readily changed by *N*/2-sodium hydroxide into 1:1'-bisphenylmethylhydrazinoindigotin, $\text{C}_{30}\text{H}_{26}\text{O}_2\text{N}_6$, yellow or yellowish-red needles, m. p. 202° (*bisphenylhydrazone*, $\text{C}_{45}\text{H}_{38}\text{N}_{10}$, yellowish-brown plates,

decomp. 165°). This reacts with cold alcoholic potassium ethoxide and methyl sulphate to form the *dimethyl ether*,



dark bluish-red plates, m. p. 105° , and its *sodium* derivative reacts with benzoyl chloride to form only a *dibenzoyl* derivative,



yellow, quadratic plates, m. p. $150-151^{\circ}$. The dibenzoyl derivative is converted into the preceding bisphenylhydrazone, decomp. 165° , by warming with phenylhydrazine, the two benzoyl groups being eliminated.

1:1'-*Bis-p-bromophenylhydrazinoindigotin*, $\text{C}_{28}\text{H}_{20}\text{O}_2\text{N}_6\text{Br}_2$, forms orange-yellow, rectangular plates, m. p. 247° (decomp.), and is converted by warm aniline and aniline hydrochloride into the *hydrochloride* of the *anil*, $\text{C}_{40}\text{H}_{30}\text{N}_8\text{Br}_2\cdot 2\text{HCl}$, blackish-blue, microscopic plates, m. p. $227-231^{\circ}$ (decomp.).

The preceding bisphenylhydrazino- and substituted bisphenylhydrazino-indigotins do not yield vat dyes on reduction, but undergo profound decomposition, the products depending on the nature of the reducing agent. The course of the reduction in acid media will be described in a later paper. The reduction of 1:1'-bisphenylhydrazinoindigotin suspended in benzene by alcoholic ammonium sulphide yields dihydroindigotin, aniline, and ammonia. Its reduction by *N*-sodium hydroxide and zinc dust in an atmosphere of coal gas for six days yields a pale yellow solution, from which is precipitated by means of atmospheric oxygen a dark blue zinc salt, probably of 1:1'-diaminoindigotin, from which is liberated by dilute hydrochloric acid the *hydrochloride* of *indigotin*-1:1'-

imide, $\begin{array}{c} \text{O} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{C} \quad \text{C} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \end{array}$, violet, rectangular plates, decomp.

185° . This base forms an *acetyl* derivative, a very sparingly soluble *sulphate*, $2\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_3\cdot\text{H}_2\text{SO}_4$, needles, and other crystalline salts, and is a true vat dye, yielding with alkaline sodium hypsulphite a yellow vat from which the imide is regenerated by means of oxygen. The preceding zinc salt yields dihydroindigotin by reduction.

C. S.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. VII. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1918, 103, 80-83. Compare A., 1918, i, 198).—The occurrence of 5-nitroglyoxaline-4-carboxylic and glyoxaline-4-glyoxylic acids, both oxidation products of histidine, among the products of the oxidation of protein, is confirmed (see Knoop, A., 1918, i, 412).

H. W. B.

Hydrolysis of Kafirin. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1918, 36, 323-334).—Kafirin, the alcohol-soluble protein of kafir (*Andropogon sorghum*), contains 21.2%

glutamic acid, 15.4% leucine, 8.1% alanine, 7.8% proline, 5.5% tyrosine, 4.3% valine, 3.5% ammonia, 2.3% phenylalanine, 2.3% aspartic acid, 1.6% arginine, 1.1% histidine, 0.95% lysine, and 0.84% cystine. Tryptophan is also present, but glycine is absent. Kafirin therefore closely resembles zein, the alcohol-soluble protein of maize, except in regard to its content of tryptophan.

H. W. B.

Proteins of the Peanut, *Arachis hypogæa*. III. The Hydrolysis of Arachin. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1918, **36**, 491—500. Compare preceding abstract). --Arachin contains 16.7% glutamic acid, 13.5% arginine, 5.5% tyrosine, 5.3% aspartic acid, 5.0% lysine, 4.1% alanine, 3.9% leucine, 2.6% phenylalanine, 2.0% ammonia, 1.9% histidine, 1.4% proline, 1.1% valine, and 0.9% cystine. Tryptophan is present, glycine absent.

H. W. B.

Chemical Study of Enzyme Action. K. G. FALK (*Science*, 1918, **47**, 423—429; from *Physiol. Abstr.*, 1918, **3**, 407). The chemical nature of enzymes is discussed in the light of the results of experiments previously published (compare A., 1917, i, 598).

H. W. B.

Studies in Fermentation. III. Pepsin and Peptic Digestion. W. BIEDERMANN (*Fermentforsch.*, 1917, **2**, 1—57; from *Chem. Zentr.*, 1918, ii, 741—742. Compare A., 1917, i, 62). A suspension of coagulated egg white in water can be employed for detecting a small amount of pepsin. The former is prepared from dried commercial egg albumin by dissolving in water, acidifying with acetic acid, adding sodium chloride, and then heating to the boiling point with continual stirring. The protein separates in very finely divided flocks, which after washing and pressing can be rubbed up with a little glycerol to form a paste, in which form it can be preserved indefinitely. A small fragment about the size of a pea in 10 c.c. of water forms a milky fluid which does not yield a perceptible sediment for several hours. On digestion with a trace of pepsin and hydrochloric acid, the turbidity quickly disappears.

Fibrin is dissolved by dilute hydrochloric acid even in the absence of pepsin. Repeated addition of fibrin results in an increased rate of solution, which appears to indicate that an autolytic or peptic enzyme is closely associated with fibrin or is formed from the fibrin by hydrolysis. If the fibrin is boiled prior to the experiment, it does not dissolve so readily in the dilute acid.

H. W. B.

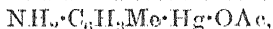
Trypsin, and a New Method of Purifying Enzymes. JOSEPH T. WOOD (*J. Soc. Chem. Ind.*, 1918, **37**, 313—315t). It has been stated by Holzberg (A., 1913, i, 662) that when a saturated solution of safranin is added to a neutral or very faintly alkaline solution of trypsin, a precipitate is formed which possesses proteolytic properties. This statement is confirmed by the author, and it

is shown that the precipitated material consists of protein matter with the safranine and the enzyme in an adsorbed condition.

Trypsin or other enzyme can be purified by dissolving in a small quantity of water and allowing the solution to soak into filter or blotting paper. After rapid drying at a low temperature, the proteins are retained more tenaciously by the paper than the enzyme, and on placing in water for a few minutes and then filtering, a solution of the enzyme is obtained practically free from protein. Such a protein-free trypsin solution does not give any precipitate with safranine.

H. W. B.

Action of Mercuric Acetate on *p*-Toluidine. I. I. VECCHIOTTI (*Gazzetta*, 1918, **48**, ii, 78--83. Compare A., 1914, i, 1063).—The interaction of mercuric acetate (1 mol.) and *p*-toluidine (1 mol.) yields *p*-toluidine-mercuriacetate,



which forms shining, white crystals, m. p. 184° ; the mercuriacetate group probably occupies the ortho-position to the amino-group. The corresponding *hydroxide*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}\cdot\text{Hg}\cdot\text{OH}$, crystallises in pale yellow plates, m. p. 212 – 213° , which begin to turn brown at about 120° ; it renders water strongly alkaline. The *chloride*, $\text{C}_7\text{H}_7\text{NClHg}$, forms prismatic needles, m. p. 170° .

T. H. P.

Physiological Chemistry.

Quantitative Evaporation of Blood Serum. (GEORGE H. BURROWS and EDWIN J. COHN (*J. Biol. Chem.*, 1918, **36**, 587–590).—The apparatus consists of an ordinary distilling flask of at least 1 litre capacity supplied with 100 grams of rather large glass pearls. The stopper carries a dropping funnel, the lower end of which extends into the bulb of the flask. The side-tube of the flask is connected with a vertical condenser, which empties into a previously weighed bottle of size suitable for trapping the evaporated and condensed water. Following this in succession is a weighed calcium chloride tower, a manometer, and a vacuum pump. The trap bottle and calcium chloride tower are immersed in ice-cold water, and ice-water should flow through the condenser jacket.

The flask and appendages having been weighed, the apparatus is exhausted to a pressure of 1 cm. of mercury, or less. The flask is immersed in a water-bath at 50° , and the liquid serum is then allowed to enter slowly through the funnel as nearly as possible at the rate at which evaporation proceeds. So treated, the serum foams largely and leaves a friable product which adheres loosely to the walls of the flask. When the desired amount of liquid has been evaporated, the cold water of the condenser jacket is replaced by

warm water and air slowly admitted through the funnel. This is followed by re-exhaustion with slight raising of the temperature of the bath. When the serum is dry, the apparatus is dismantled and the parts weighed. Serum contains about 9% of solids, which, as thus obtained, dissolve readily in water, yielding a slightly turbid solution.

H. W. B.

The Action of Ferric Thiocyanate on Normal Human Serum. ARTHUR VERNES and ROGER DOURIS (*Compt. rend.*, 1918, **167**, 972—974).—The reagent prepared by the action of ammonium thiocyanate or ferric chloride is added to a series of tubes containing 0.4 c.c. of diluted serum, in diminishing dilutions. The first tubes show no precipitation, then follow a series of tubes in which precipitation takes place, and these are followed by another series with no precipitation.

S. B. S.

Mineral Metabolism in Experimental Acidosis. KINGO Goro (*J. Biol. Chem.*, 1918, **36**, 355—376).—The daily administration of hydrochloric acid to a rabbit during a period of from one to four weeks was accompanied by an increase in the urinary excretion of phosphoric acid. Subsequent investigation showed that the muscles were deficient in phosphorus, sodium, and potassium, and the bones in calcium carbonate. The fat content of the skeleton was also greatly reduced. These results indicate that in acid intoxication after the carbonates in the body fluids have been neutralised, the alkali phosphates of the muscles and the calcium carbonate of the bones are drawn on in the attempt to maintain the hydrogen-ion concentration of the body tissues at the normal level.

H. W. B.

Comparative Metabolism of certain Aromatic Acids.
II. Fate of *p*-Hydroxybenzoic Acid and *p*-Hydroxyphenylacetic Acid in the Organism of the Monkey. CARL P. SHERWIN (*J. Biol. Chem.*, 1918, **36**, 309—318. Compare A., 1917, i, 603).—Feeding experiments on a monkey (*Macacus rhesus*) indicate that in relation to the process of the metabolism of the aromatic amino-acids, the monkey stands in the same position as other lower animals and thus differs from man. The monkey excretes the *p*-hydroxybenzoic acid in the urine in an uncombined state, whilst a partial combination with glycine takes place in the human organism. On the other hand, *p*-hydroxyphenylacetic acid is partly excreted as *p*-hydroxyphenylaceturic acid in the case of the monkey and lower animals, but is excreted in an uncombined form in man.

H. W. B.

Metabolic Changes induced by the Administration of Guanidine Bases. V. **Change of Phosphate and Calcium Content in Serum in Guanidine Tetany and the Relation between the Calcium Content and Dextrose in the Blood.** C. K. WATANABE (*J. Biol. Chem.*, 1918, **36**, 531—546. Compare A., 1918, i, 327).—The administration of guanidine to rabbits produces a condition of severe acidosis with the retention of phosphates, a

decrease of calcium in the blood, and a hypoglycaemia. After the extirpation of the parathyroids in the rabbit, phenomena and symptoms are observed which are similar to those occurring after the administration of guanidine. Since there is a large increase in the guanidine bases in the blood in parathyroid and in idiopathic tetany, it is possible that the fundamental cause of tetany is the increased formation of guanidine brought about by the disturbance of the function of the parathyroids.

H. W. B.

Influence of Protein Feeding on the Concentration of Amino-acids and their Nitrogenous Metabolites in the Tissues. H. H. MITCHELL (*J. Biol. Chem.*, 1918, **36**, 501—520).—The concentration of amino-acids, ammonia, and urea in the tissues of rats is comparable to that in the tissues of other mammals. In the young, growing animal the concentration of the amino-acids in the tissues is considerably higher than in the adult animal, due possibly to the greater metabolic activity of the young as compared to the adult tissues. The effect of feeding with protein depends also on the age of the animal; in young rats the concentration of the amino-acids and urea in the tissues is increased, whilst in the adult animal no or only a slight increase can be detected.

H. W. B.

Animal Calorimetry. XV. Further Experiments Relative to the Cause of the Specific Dynamic Action of Protein. H. V. ATKINSON and GRAHAM LUSK [with G. F. SODERSTROM] (*J. Biol. Chem.*, 1918, **36**, 415—427. Compare Lusk, A., 1915, i, 614).—The administration of hydrochloric acid to a dog causes a slight increase in the basal metabolism, but a further increase is not observed when aspartic acid is simultaneously given. Aspartic acid, like glutamic acid, does not therefore exert any specific dynamic action. Asparagine and glycine behave very differently in metabolism, the former being without specific dynamic action, whilst the latter exerts the most powerful specific dynamic action of any of the amino-acids in protein which have been thus far tested. Therefore, the hypothesis of Grafe (*Deutsch. Arch. Klin. Med.*, 1915, **118**, 1) that the specific dynamic action of protein is due to the amino-radicles of the amino-acids is shown to be incorrect. Neither succinic acid nor acetamide is found to increase the heat production of the animal. The authors draw the conclusion that the processes of deamination and urea formation have nothing to do with the specific dynamic action of protein.

H. W. B.

Penetration of Neutral Salts into [Animal] Cells. WILHELM VON MOELLENDORFF (*Kolloid Zeitsch.*, 1918, **23**, 158—163).—A number of experiments on the penetration of solutions of sodium chloride, manganese sulphate, uranium nitrate, and potassium sulphate into liver and kidney cells of animals are described. The experiments show that sufficient of the salts penetrate to produce an intracellular precipitation of the acid colour substances contained in the cells. This precipitation is identical with the action of neutral

salts on semi-colloids and is characterised as a diminution of the dispersion. The process indicates that the cell walls are permeable to neutral salts. The process is in keeping with the theory of a sponge-like structure for protoplasm. J. F. S.

Synthetic Capacity of the Mammary Gland. I. Can this Gland Synthesise Lysine? E. B. HART, V. E. NELSON, and W. PITZ (*J. Biol. Chem.*, 1918, **36**, 291--307).—Rats fed on a lysine-free diet of zein and tryptophan with non-nitrogenous substances are able to give birth to their young, but appear to be unable to rear them. It is considered that these results are due to the failure of the mammary glands of the rats to produce sufficient milk, owing to the absence of the lysine necessary for the formation of the protein normally present in rat's milk. H. W. B.

Vitamine Studies. II. Does Water-soluble Vitamine Function as a Catalase Activator? R. ADAMS DUTCHER and FERDINAND A. COLLATZ (*J. Biol. Chem.*, 1918, **36**, 547--550. Compare A., 1918, i, 561).—Vitamine extracts do not increase the catalytic activity of extracts of liver. The vitamine in the body does not act as a direct activator of catalase, but seems to stimulate the organism to greater production of the enzyme. H. W. B.

Vitamine Studies. III. Curative Properties of Honey, Nectar, and Maize-pollen in Avian Polyneuritis. R. ADAMS DUTCHER [with L. V. FRANCE] (*J. Biol. Chem.*, 1918, **36**, 551--555. Compare preceding abstract).—Honey contains a small amount of the water-soluble vitamine, but the amount is so small that its curative effect can only be observed after concentration of the vitamine by adsorption with siliceous earth. Nectar appears to be almost free from vitamines, but maize-pollen is relatively rich in this respect, small amounts of pollen extract being sufficient to cause the recovery of pigeons in the last stages of polyneuritis. It is possible that it is the presence of pollen grains in ordinary honey which confers on it its small curative power over polyneuritis. H. W. B.

Quinine in Animal Tissues and Liquids, with Methods for its Estimation. W. RAMSDEN, I. J. LIPKIN, and E. WHITLEY (*Ann. Trop. Med. Parasitol.*, 1918, **12**, 223--258. Compare Ramsden and Lipkin, A., 1918, ii, 251; Hartmann and Zila, A., 1918, i, 328).—The method previously described by Ramsden and Lipkin is applicable to the estimation of quinine in most tissues, but not in liver and brain. Given in large doses, the alkaloid accumulates in most tissues (particularly the suprarenals and kidneys) much more than in the blood, where three-fourths is in the serum but scarcely any in the red corpuscles; 90% of an intravenous dose leaves the blood in the first minute after injection. Quinine resists putrefaction in urine and faeces, but is rapidly attacked post mortem by the liver, presumably in a manner identical with the normal fermentative process of quinine metabolism during life. In a succession of large doses by the mouth more than 90% may be so metabolised. In

man there is considerable idiosyncrasy, both as regards the rate of excretion and the concentration in the blood; high concentration in the blood is associated with the symptoms of quinine intoxication. Quinotoxine is attacked by the liver like quinine, but some at least is excreted unchanged by the urine. G. B.

Creatinuria. I. Exogenous Origin of Urinary Creatine.

II. STEENBOCK and E. G. GROSS (*J. Biol. Chem.*, 1918, **36**, 265—289).—Experiments on pigs are described, the results of which indicate that creatine is formed from a precursor or precursors in the protein molecule. Urinary creatine has an exogenous origin only when the protein in the food happens to contain a large proportion of the creatine precursor. Feeding with excess of a protein containing a relatively small proportion of the creatine precursor may result in an inhibition of the production of creatine, on account of the accompanying diminution in protein katabolism effected by the agency of the non-nitrogenous portion of the protein of the food. In the discussion of the results attempts are made to reconcile the numerous apparently contradictory conclusions arrived at by other workers on this subject. H. W. B.

Method for the Identification of certain Carbamido-acids in the Presence of Amino-acids and of Urea. ALICE RONDE (*J. Biol. Chem.*, 1918, **36**, 467—474).—The method consists in decomposing the urea by urease, and then extracting the carbamido-acids, after acidifying with phosphoric acid, by means of ethyl acetate. The extract is then distilled with steam and the aqueous residue clarified with charcoal and then concentrated to small bulk. The crystals of carbamido-acid which separate are identified by the melting point, etc.

A method for the quantitative estimation of these acids by the Van Slyke process is based on the fact that the anhydrides formed from them are not decomposed by nitrous acid. The difference in the volumes of gas evolved before and after boiling the carbamido-acid solution with hydrochloric acid is a measure, therefore, of the amount of carbamido-acid present.

Applying these methods, it is found that after the injection of amino-acids into cats, carbamido-acids cannot be detected in the urine, whilst injected carbamido-acids are excreted in an unaltered form. Conjugation of amino-acids with urea preparatory to excretion does not seem, therefore, to occur in the animal organism. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Autolysis of Starch. W. BIEDERMANN (*Fermentforsch.*, 1918, **2**, 200; from *Chem. Zentr.*, 1918, ii, 738. Compare A., 1917, i, 62).—Boiled starch solutions after some weeks become infected with a bacterium which forms a sulphur-yellow pigment and hydrolyses

the starch to dextrose. The bacterium is possibly identical with, or at least closely related to, Schardinger's *Bacillus macerans*. The previously recorded autolysis of starch was probably due to infection with this micro-organism.

H. W. B.

Azofication. J. E. GREAVES (*Soil Sci.*, 1918, 6, 163—217).—A résumé of the literature on the subject of nitrogen fixation by *Azotobacter* and *Clostridium pasteurianum*. A full bibliography is appended.

W. G.

Influence of certain Conditions on the Comparative Consumption of Dextrose and Lævulose by Sterigmatocystis nigra, starting from Sucrose. MARIN MOLLIARD (*Compt. rend.*, 1918, 167, 1043—1046).—Using a culture liquid in which the nitrogen is entirely supplied by one ammonium salt and the ratio nitrogen:carbon is 1:16, it is found that the ratio of dextrose to lævulose consumed is considerably increased by the presence of acid. Similarly, the ratio dextrose to lævulose consumed is increased if the ratio nitrogen:carbon is diminished to 1:160. In each of these cases, the weight of mycelium obtained in a given time is also diminished. It is considered that lævulose plays the principal part in the building up of the tissues.

W. G.

Capacity of Alcohols and Acids to Sustain the Growth of Yeasts and other Common Fungi. TH. BOKORNY (*Allg. Brau Hopf. Zeit.*, 1917, 747; from *Bied. Zentr.*, 1918, 47, 191).—The author has collected information regarding the behaviour of fungi, yeasts, and bacteria when cultivated in media containing various alcohols and acids. All acids exert an inhibiting action on fermentation when the concentration is increased to a certain limit, which differs for each substance. Formic and oxalic acids are specially toxic. Bases are more poisonous than acids towards yeast.

H. W. B.

Quantitative Estimations of the Enzymic Activity of Living Cells. I. H. EULER, O. SVANBERG, and S. HEINTZE (*Fermentforsch.*, 1918, 2, 194—199; from *Chem. Zentr.*, 1918, ii, 746).—At 16°, an increase in p_H from the optimum for yeast invertase (5.07 to 4.67) to 7.7 reduces the activity of the invertase from 0.067 to 0.007.

H. W. B.

Influence of certain Substances Extracted from Yeast by Alcohol on the Activity of the Yeast Enzymes. EMIL ABDERHALDEN and H. SCHAUAMANN (*Fermentforsch.*, 1918, 2, 120—151; from *Chem. Zentr.*, 1918, ii, 737—738).—An extract of yeast, prepared by boiling with 10% sulphuric acid and subsequently treating with alcohol, exerts an accelerating action on the enzymic cleavage of sucrose and maltose and on the fermentation of dextrose, lævulose, and particularly galactose by yeast. The fermentation of lactose is not affected. The activity of carbonylase is increased. The accelerative action of the extract is observed, not only with living yeast, but in the cases of dried yeast and pressed yeast juice. Various fractions can be prepared from

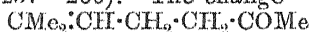
the extract possessing diverse degrees of activating power, one of the more powerful being termed "eutonin." This latter substance is prepared by precipitation of the alcoholic extract with acetone, and is completely free from phosphorus. The author suggests that vitamins may resemble these extracted substances in exerting an activating influence on certain enzymic processes in the body.

H. W. B.

Behaviour of Yeast towards various Carbohydrates in various Concentrations, and the Effect of the Addition of Amino-acids on the Fermentation. EMIL ABDERHALDEN (*Fermentforsch.*, 1916, 229; from *Bied. Zentr.*, 1918, 47, 190).—The extent of alcoholic fermentation is not affected when the concentration of the sucrose in the solution is increased from 10 grams to 30 grams per 250 c.c. The loss in weight is greater when alanine is added to the sucrose solution. When dextrose is substituted for sucrose, the extent of fermentation is found to vary with the concentration of the carbohydrate. When dried yeast is employed, a distinct latent period precedes the onset of fermentation.

H. W. B.

Phytochemical Reductions. XIV. Hydrogenation of a Ketone by Yeast. Change of Methylheptenone into the Corresponding Heptenol. C. NEUBERG and A. LEWITE (*Biochem. Zeitsch.*, 1918, 91, 257—266).—The change



into $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ takes place to the extent of about 10%. The product is sometimes laevorotatory and at other times dextrorotatory. There is produced at the same time an equimolecular proportion of acetaldehyde. The ketone appears to compete with this product, formed as an ordinary intermediary product of alcoholic fermentation, for the available hydrogen.

S. B. S.

Excitation of Ferment Action. WOLFGANG WEICHARDT and HERMANN APITZSCH (*Biochem. Zeitsch.*, 1918, 90, 337—347).—A criticism of certain statements in literature with regard to excitation of ferment action, with some demonstrations of sources of error in methods of manipulation in experiments on which certain statements are founded. These refer more especially to the measurement of catalase action volumetrically, to the difficulties of measuring the same amounts of catalase (or blood), and to the errors in the estimation of the action of urease due to the neglect of hydrolysis of carbamide while distilling off the ammonia.

S. B. S.

The Influence of Aluminium on the Germination of Seeds and the Development of Plants. JULIUS STOKLASA with J. ŠEBOR, W. ZDOBNICKÝ, F. TÝMICH, O. HORÁK, A. NĚMEC, and J. CWACH (*Biochem. Zeitsch.*, 1918, 91, 137—223).—This communication contains a very detailed account of the action of aluminium, manganese, and iron on the germination of seeds and the development of the plants. It indicates, generally, that very

small amounts of aluminium salts exert a favourable influence on the germination of seeds, whereas larger amounts exert a toxic action. Similar remarks apply to salts of manganese. When large amounts of manganese salts exert a toxic action, an antagonistic effect can be produced by aluminium salts when the concentration of the latter is not too high, and the toxic effect of both ions comes into play. A study of the action of these various salts when used in the nutrient solutions for growing plants indicated that aluminium is very toxic to xerophytes, whereas the hydrolytes and hygrophils show a considerable resistance. As regards the mesophytes, a toxic action could be determined in the case of iron ions which could be antagonised by aluminium. Aluminium and manganese ions in sufficiently low concentrations, both together or alone, produce a favourable effect on growth; higher concentrations act toxically. There is no antagonistic action as regards toxicity of iron and manganese. The authors deduce from their results a mathematical expression for the growth curves, and develop a general theory of the action of chemical reagents on growth. Measurements were made of the electrical conductivities of the salts employed, and comparisons instituted between the intensity of action of the various ions and the dissociation grade of the salts; a considerable parallelism was found to exist between this physiological intensity of action and the conductivities of the salt solutions. S. B. S.

Catalase and Oxydase Content of Seeds in Relation to their Dormancy, Age, Vitality, and Respiration. WILLIAM CROCKER and GEORGE T. HARRINGTON (*J. Agric. Res.*, 1918, 15, 137—174).—The concentration of solutions of hydrogen peroxide may readily be measured by determining the volume of oxygen liberated on the addition of an excess of powdered seeds containing plant catalase. Similarly, the catalase activity of seeds may be measured by using an excess of hydrogen peroxide, but in this case the latter solution must first be made neutral to phenolphthalein by the addition of $N/10$ -sodium hydroxide. The authors have carried out a general investigation as to the conditions affecting catalase and oxydase activity of seeds, and find that in certain seeds there is a close correlation between catalase activity and respiratory intensity, but no correlation between these two factors and the vitality of the seeds or the vigour of the resulting seedlings. They find that general conclusions cannot be drawn as to the catalase behaviour in all seeds, but it seems probable that seeds can be separated into several physiological types, for each of which more or less general conclusions can be drawn. Catalase activity of seeds seems to agree more closely and generally with physiological behaviour than does oxydase activity. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. G.

Distribution of the Mineral Elements and Nitrogen in the Etiolated Plant. G. ANDRÉ (*Compt. rend.*, 1918, 167, 1004—1006).—The author has investigated the proportions of

mineral matter and nitrogen which pass, during etiolation, from the cotyledons into the plantule in seeds germinated in the dark in an inert medium. The seeds used were white haricot, germinated in sand previously extracted with acid and calcined. After twenty-five days, the stems being 30—35 cm. in length, the plants were removed and their roots washed. Their cotyledons were separated from the stem and roots and weighed separately, and then analysed. The major portion of the calcium remained in the cotyledons, whilst the magnesium, and to a still greater extent the potassium, had migrated to the roots and stem. Nearly 75% of the phosphoric acid and nitrogen were transported from the cotyledons to the plantule, and the migration of the sulphur was very similar.

W. G.

Mechanism of Assimilation Processes. K. SCHAUM (*Ber.*, 1918, 51, 1372—1375).—The conclusions recorded by Willstätter and Stoll (*A.*, 1918, i, 207) had been drawn previously by the author (*Sitzungsber. Ges. Beförd. gesamt. Naturwiss. Marburg*, 1907, 158).

C. S.

Colloidal Properties of Protoplasm. Imbibition in Relation to Growth. FRANCIS E. LLOYD (*Trans. Roy. Soc. Canada*, 1917—18, [iii], 11, 133—139).—Living protoplasm, as such, behaves towards acids and alkalis in a manner sufficiently like that of gelatin to warrant the view that imbibition is a factor in growth. The results in growth are called forth by much lower concentrations of the reagents; this is probably due to the different nature of the emulsoids involved.

J. F. S.

Conductivity as a Measure of Permeability. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, 36, 485—487).—Experiments are described which are designed to elucidate whether when an electric current passes through a tissue, any of the current passes through the protoplasm or all through the intercellular substance. Employing a green marine alga (*Ulva*) and a marine flowering plant (*Zostera*), both with cellulose walls, it is found that after killing by methods which do not produce irreversible changes in the properties of cellulose, the conductivity rises to a constant value and is not thereafter affected by exposure to reagents which produce great alterations in the conductivity of living tissues. Moreover, the temperature-coefficient of the electrical conductivity of living tissue differs from that of dead tissue, and the effect of placing a tissue in contact with a strong calcium chloride solution is not an increase in the conductivity, but a decrease on account of the diminished conductivity of the protoplasm killed by the salt more than counterbalancing the increased conductivity of the intercellular tissues. The alterations of conductivity observed in living tissue are due, therefore, to changes in the protoplasm, and not to changes in the non-living intercellular substance, and as the results obtained by the electrical method are in complete agreement with those obtained by other methods for measuring permeability, such as exosmosis,

diffusion through membranes of living tissue, etc., the author draws the conclusion that the electrical conductivity is a measure of the permeability of the protoplasm of the cell. H. W. B.

Effect of Diffusion on the Conductivity of Living Tissue. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 489—490).—Electrolytes with univalent cations usually produce an increase in the electrical conductivity of living tissues, whilst those with bi- or tri-valent cations first diminish and then increase the conductivity. Certain apparent exceptions to this rule have been noted, and these are now shown to be due to the effect of diffusion. Thus, on transferring tissue of *Laminaria* from sodium chloride to rubidium chloride solution of the same conductivity, the molecules of sodium chloride diffuse out of the tissue more rapidly than the larger molecules of rubidium chloride can diffuse inward. Hence there is a temporary deficiency of salt in the tissue, and the conductivity accordingly falls. Reverse effects are produced on transference into lithium chloride solutions. H. W. B.

Method of Measuring the Electrical Conductivity of Living Tissues. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **36**, 557—568).—Various types of apparatus are figured and described which permit of the measurement of the electrical conductivity of pieces of living tissue or of intact organisms. Successive measurements do not vary more than 1% from the mean value. H. W. B.

The Absorption Curve of the Green Colouring Matter in Living Leaves. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 73—85).—The absorption curve has been determined by the thermoelectric method for the green pigments in a living leaf of *Tradescantia*. A very slight absorption occurs in the green part of the spectrum, which increases towards the red and the violet ends, reaching a maximum in the violet, which is greater than that occurring in the red. Towards the red end of the spectrum the absorption curve reaches a maximum point between *B* and *C*, and then falls rapidly towards the ultra-red. H. W. B.

Significance of the Wave-length for Starch-formation [in the Green Leaf]. A. URSPRUNG (*Ber. Deut. bot. Ges.*, 1918, **36**, 86—100. Compare preceding abstract).—A comparison of the absorption curve with one indicating the extent of formation of starch in the green leaf reveals a close parallelism extending from the ultra-red to the green part of the spectrum. From this point towards the violet, marked divergence is observed; the absorption increases to a maximum, whilst the starch-formation greatly diminishes. It is probable that the latter phenomenon is occasioned by the action of the ultra-violet light on the stomata, which results in the reduction of the supply of carbon dioxide for photo-synthetic purposes. In a few experiments with leaves containing no stomata,

the parallelism between absorption and starch-formation could be established as far as the bluish-violet part of the spectrum.

H. W. B.

Microchemistry of Plants. X. Siliceous Bodies in the Epidermis of *Campelia Zanonii*, Rich. XI. Crystalline Carotin in the Cup of *Narcissus poëticus*. HANS MOLISCH (*Ber. deut. bot. Ges.*, 1918, **36**, 277—281, 281—282).—Siliceous bodies, similar to those discovered by Möbius (*Wiesner-Festschrift*, Vienna, 1908, p. 81) in the leaves of *Callisia repens*, are present in the epidermis of *Campelia Zanonii*. They occur in small cells in the leaves and stalks, and are insoluble in acids, except hydrofluoric acid. When the leaf is immersed in phenol solution or in Millon's reagent, the bodies assume a peculiar red hue, which renders them very apparent. These two *Commelina*, therefore, are related, not only botanically, but also in a pronounced chemical manner.

The red colour in the rim of the cup of *Narcissus poëticus* is found to be due to the presence of accumulations of carotin crystals in the cells.

H. W. B.

The Phenol of the Leaves of *Coleus amboinicus*, Lour (*C. Carnosus*, Hassk.). F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 355—356; *Pharm. Weekblad*, 1918, **55**, 1470—1472).—The essential oil of *Coleus amboinicus* contains a phenol which the author has identified as carvacrol.

W. G.

Presence of Hydrogen Cyanide in a Fern, *Cystopteris alpina*. MARCEL MIRANDE (*Compt. rend.*, 1918, **167**, 695—696).—The fern, *Cystopteris alpina*, Desv., contains in its leaves a cyanogenetic glucoside which under the influence of an enzyme, also contained in the plant, is hydrolysed, and yields hydrogen cyanide and benzaldehyde. The proportion of hydrogen cyanide given by the leaves is lowest in the early part of September (for example, 0·011%).

C. A. M.

Production of Glycine by *Isaria densa*. MARIN MOLLIARD (*Compt. rend.*, 1918, **167**, 786—788).—The fungus *Isaria densa*, when cultivated on gelatin decomposes it, giving glycine, the yield of this amino-acid being equivalent to 33% of the gelatin decomposed, whereas by acid hydrolysis gelatin only yields 16·5% of glycine. Similarly, this fungus decomposes fibrin, giving 38% of glycine, and also ovalbumin, serum-albumin, and casein, giving on an average 33·6% of glycine.

W. G.

Sterilised Poppy Juice. L. REUTTER DE ROSEMONT (*Schweiz. Apoth. Zeit.*, 1918, **56**, 55—56; from *Chem. Zentr.*, 1918, ii, **89**, 736—737).—The results indicate that certain alkaloids exist pre-formed in poppy juice and are not the products of subsequent fermentation processes. On distillation in a vacuum, poppy juice

gives off formic and acetic acids, and, after subsequent treatment with sodium hydroxide, ammonia, pyrrolidine, and methylpyrrolidine. By extraction of the tarry residue, several basic substances, including codeine but not morphine, are obtained. Light petroleum extracts pyrrolidine, benzene, a yellow *liquid*, $(C_8H_9O_4N)_x$, *aureichloride*, m. p. 231° , chloroform, a yellowish-brown *powder*, $(C_3H_7O_9N)_x$, and amyl alcohol, a solid *alkaloid* $(C_9H_9O_3N)_x$. The residue is soluble in dilute hydrochloric acid, and from the solution sodium hydroxide precipitates a colourless *substance*, $(CHO_3N)_x$. Lactic, meconic, and oxalic acids, together with dextrose, were also detected in the original juice. H. W. B.

Vegetable and Animal Fats and Waxes. II. ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, **103**, 84–86. Compare A., 1918, i, 56).—The solid fat isolated from rice bran does not contain any glycerol, whilst the liquid oil contains only about 1.7%. H. W. B.

Oxydases: with Special Reference to their Presence and Function in the Sugar-cane. RAMJI NARAIN (*Agric. J. India*, 1918, 47–64).—Laccases and aldehydase are found to be present in the cane, but tyrosinase is absent. The author finds that the direct guaiacum reaction depends more on the presence of a peroxide than on that of catechol. As a preservative for oxydases, chloroform is far more satisfactory than either ether or toluene. In the cane the lower portions show a greater oxydase activity than the upper portions, and thus the oxydases are stronger in that part of the plant where the sugar is stored. Similarly, the leaf and the adjoining green portion of the cane are richer in oxydase than the stem. The oxydases are not destroyed by boiling the extract containing them for fifteen minutes, although they take some time to recover their activity after cooling. Similarly, a reducing agent such as hydrogen sulphide only temporarily inhibits their activity but does not destroy it permanently. The author considers that oxydases are not enzymes in the true sense of the word. W. G.

Gaseous Products of the Putrid Fermentation and the Odour of Truffles. I. GUARESCHI (*Gazzetta*, 1918, **48**, ii, 98–106).—The gaseous or highly volatile products emitted during the putrefaction of truffles are mostly absorbable by soda lime (compare A., 1916, ii, 324, 562). Those not so absorbed have the odour of the fresh truffle, such odour being due to one or more gases or volatile compounds, which are formed by the putrefactive alteration of the proteins, but are not yet identified. T. H. P.

Action of Coal Gas on Plants. IV. Action of Coal Gas on the Root Systems of Trees. Cause of the Action of the Gas. C. WEHMER (*Ber. Deut. bot. Ges.*, 1918, **36**, 140–150. Compare A., 1917, i, 618).—The experiments on the effects produced by passing gas through soil containing the roots of plants have been

extended to small trees in pots. It is found that the effect produced is dependent on the season of the year in which the experiment is performed; it completely kills the tree in the spring; in autumn the leaves fall off, but the tree remains alive, whilst in winter no pernicious effect is observable. When the soil is replaced by a solution of salts, similar toxic effects are observed. The toxicity appears to be due to one or more constituents of the gas, and not to mere absence of oxygen. Any treatment of the gas which removes its peculiar odour also abolishes its toxicity, a result which seems to show that the toxic agent is that constituent of the gas which confers on it its characteristic odour. H. W. B.

Soil Acidity as Affected by Moisture Conditions of the Soil. S. D. CONNER (*J. Agric. Res.*, 1918, 15, 321—329).—The acidity of acid soils, kept under different conditions of moisture in pots for a year, varied with the different conditions of moisture for a given soil. Soils rich in organic matter showed the greatest acidity after being kept fully saturated, whilst soils poor in organic matter showed the greatest acidity after being kept half-saturated. The potassium nitrate extract from the fully saturated soils contained more soluble ferrous iron and manganese, but less aluminium, than the other soils. Thus the measurable acidity of acid soils varies to a large degree under different conditions of moisture and aeration, but this variation is due to chemical rather than to physical changes in the soil. W. G.

Determining the Absolute Salt Content of Soils by Means of the Freezing-point Method. GEORGE J. BOUYOUCOS and M. M. MCCOOL (*J. Agric. Res.*, 1918, 15, 331—336).—The authors find that at a comparatively high content of moisture, the influence of the unfree water on the concentration of the soil solution is practically negligible. The freezing-point method can therefore be used to determine the absolute salt content of soils by bringing them to a suitable content of moisture before determining the depression of the freezing point. [For details, see *J. Soc. Chem. Ind.*, 1919, February.] W. G.

Hydrogen-ion Concentration—Soil Type—Common Potato Scab. LOUIS J. GILLESPIE and LEWIS A. HURST (*Soil Sci.*, 1918, 6, 219—235).—The authors find that the electrometric method (compare Gillespie, A., 1916, i, 303) and the colorimetric method of Clark and Lubs (compare *J. Bact.*, 1917, 2, 1, 109, 191) for determining hydrogen-ion concentration of soils give results which are in agreement within the limits of experimental error. It is necessary to add 1 or 2 c.c. of water to each gram of air-dry soil, but this addition of water does not seem to be a serious limitation. From an examination of a large number of soils the authors find a close correlation between the hydrogen-ion exponent and the occurrence of common potato scab. With an exponent below 5.2, scab seldom appears, but with exponents much above this figure the potatoes are generally scabbed. W. G.

Chlorine Index as a Comparative Measure of the Richness of Soils in Humus. L. LAPICQUE and E. BARBÉ (*Compt. rend.*, 1919, 168, 118—121).—The authors find that the amount of an aqueous solution of sodium hypochlorite decomposed in a given time by a given volume of soil varies considerably with the soil taken, and that this estimation forms a rough method of placing the soils in the order of their probable richness in humus, the volume of chlorine liberated varying directly with the humus content of the soil. W. G.

Importance of Mould Action in the Soil. SELMAN A. WAKSMAN (*Soil Sci.*, 1918, 6, 137—155).—Moulds have been isolated in large numbers from cultivated and uncultivated soil. By the growth of their mycelia, changes in the organic and inorganic constituents of the soil are brought about, but no nitrification or fixation of nitrogen is effected. Not much ammonia is produced in the presence of available carbohydrate as a source of energy, as it is absorbed in the formation of mould protein, but in the absence of carbohydrate considerable amounts of ammonia are left in the soil. Carbohydrates are decomposed with the formation of carbon dioxide. Moulds exercise an unfavourable effect on soil fertility in that they compete with green plants for available nitrogen compounds. On the other hand, they exercise also a beneficial effect on account of their large production of enzymes and acids, which produce further changes in soil constituents favourable to the growth of green plants. [See *J. Soc. Chem. Ind.*, 1919, February.] J. H. J.

Nitrogen Compounds in Rain and Snow. FRANK T. SHUTT and R. L. DORRANCE (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], 11, 63—72).—A series of analyses of snow and rain which have fallen in or near Ottawa during the years 1908—1917 is recorded. The analyses deal with the nitrogen compounds, and are expressed as parts of nitrogen per million as (i) free ammonia, (ii) albuminoid ammonia, (iii) nitrates and nitrites. The average of these for the ten years is 0.461 nitrogen as free ammonia, 0.138 as albuminoid ammonia, 0.277 as nitrite and nitrate. This corresponds with 6.583 lb. of nitrogen per acre. A further analysis of the results for the various months is also given, from which it is shown that snow is decidedly poorer in all forms of nitrogen compounds than rain (compare A., 1915, i, 636). J. F. S.

Composition of the Waters of the Inter-Mountain Region. J. E. GREAVES and C. T. HIRST (*J. Ind. Eng. Chem.*, 1918, 10, 1001—1004).—Analyses of a large number of river waters are recorded, the majority of which are used for irrigation purposes. Whilst some of the waters are free from objectionable constituents, others, although good at their source, were found to contain large quantities of alkali sulphates, etc., after flowing through a district rich in soluble salts. The effect of these saline waters on vegetation is discussed. W. P. S.

Organic Chemistry.

Products of the Action of the Silent Electric Discharge on Acetylene. H. P. KAUFMANN (*Annalen*, 1918, 417, 34—59).—After giving a résumé of previous work on this subject, the author describes in detail his own apparatus, photographs of which are given. The essential part consists of two concentric glass tubes about 75 cm. long having a space of 5 mm. between their walls. The interior of the inner tube is silvered, and through it a rapid stream of cold water is passed. The outer tube is immersed in dilute sulphuric acid, in which is a cooling coil. Electrical connexion is made between the silvered surface and the sulphuric acid with the poles of an induction coil operated by a high-frequency machine (230—250 volts, 2.5—3 amperes). A stream of acetylene is passed between the tubes, and all air in the apparatus must be completely displaced by the acetylene before the silent discharge is passed. When the reaction vessel is allowed to get warm, the product is a mixture of a solid and a liquid, but if the vessel is kept cold, a liquid product only is obtained, which collects at the bottom of the vessel at the rate of about 30—50 grams per hour. The liquid is a brown, viscous oil having an unpleasant odour. It has the composition $(C_2H_2)_x$ and is very unstable, changing by warming, by keeping in solution, or by the attack of almost any chemical agent into the solid, which appears to be identical with that described by de Wilde (*Ber.*, 1874, 7, 357). The liquid decomposes and carbonises above 100° , but a small quantity distils at $70^\circ/10$ mm., which is a mixture of several substances; the residue in the flask changes to a plastic mass, which ultimately becomes brittle.

The solid product obtained in the warm reaction vessel is more conveniently obtained by warming a solution of the liquid product in ether at about 60° . It is a pale yellow, odourless powder, which is insoluble in all solvents.

Both the liquid and the solid rapidly absorb oxygen, and it is only during such absorption that they produce any action on a photographic plate.

The solid does not react with a dilute solution of bromine under ordinary conditions, but is attacked by more concentrated solutions, hydrogen bromide being evolved. The liquid readily absorbs bromine, best in solution in carbon tetrachloride, a pale yellow powder being obtained, the composition of which appears to be $(C_2H_2Br)_{28}$, assuming it to be an individual substance.

A 98% alcoholic solution of silver nitrate produces with a solution of the liquid product in carbon tetrachloride a pale yellow, flocculent precipitate of a silver derivative, which explodes on heating; the presence of a :CH group in the liquid product is thus indicated.

By boiling with 47% nitric acid, the solid product yields nitro-

compounds of high molecular weight, together with a little benzoic acid. By oxidation with alkaline permanganate, the liquid product yields benzoic, *isophthalic*, and *terephthalic* acids. The same three acids are obtained, although with much greater difficulty, by oxidising the solid product with alkaline permanganate. C. S.

Allyl Alcohol. M. J. STRITAR (*Monatsh.*, 1918, **39**, 617—626). — Bromine is quantitatively absorbed by allyl alcohol whether the former is in excess or not; the reaction is suitable for the exact quantitative estimation of allyl alcohol, which may be effected either by direct titration with bromine water until a permanent yellow coloration is obtained, or by treating the acidified aqueous solution of the alcohol with an excess of bromide-bromate solution, followed by addition of potassium iodide and titration of the liberated iodine with sodium thiosulphate (compare Stritar and Zeidler, A., 1904, ii, 686).

When bromination is effected in dilute aqueous solution, about 47·5% of the added bromine is immediately and spontaneously eliminated as hydrogen bromide. Elimination of the second bromine atom (exchange for hydroxyl) occurs slowly and incompletely in acid solution, small amounts of acraldehyde being formed. Practically the whole of the bromine is removed when the product is heated under pressure at 100° with the calculated quantity of potassium hydroxide (or with a 10% excess); the yield of glycerol is about 97% of that theoretically possible. The small deficiency is caused by the formation of a volatile, saturated bromide which is fairly resistant to alkali.

H. W.

The System Ethyl Ether—Chloroform. A. SMITS and V. S. F. BERCKMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 401—404). — A melting-point curve for various mixtures of ethyl ether and chloroform has been determined. The curve shows that an equimolecular compound is formed (m. p. $-94\cdot4^\circ$), as was stated by Dolezalek and Schulze (A., 1913, ii, 108), but, in addition, two other compounds, (i) a compound made up of two molecules of chloroform and one molecule of ethyl ether (m. p. $-93\cdot3^\circ$), and (ii) one made up of two molecules of ethyl ether and one of chloroform. The latter compound does not melt, but dissociates at $-113\cdot8^\circ$ into the equimolecular compound and ethyl ether.

J. F. S.

Physical Constants of "Mustard Gas" [$\beta\beta'$ -Dichloroethyl Sulphide]. LEASON H. ADAMS and ERSKINE D. WILLIAMSON (*J. Washington Acad. Sci.*, 1919, **9**, 30—35). — The compressibility of $\beta\beta'$ -dichloroethyl sulphide has been determined over the pressure range 392—1713 megabars at $31\cdot5^\circ$ by the method previously described (this vol., ii, 98). The compressibility is represented by the equations $\Delta v/v_0 = 4\cdot24 \times 10^{-5}(P - P_0) - 6\cdot3 \times 10^{-5}(P - P_0)^2$ and $-\Delta v/v_0 = 0\cdot118(1 - e^{-0\cdot364 \times 10^{-3}(P - P_0)})$. Differentiating this, the relationship $-dv/dP = 49\cdot5e^{-0\cdot364 \times 10^{-3}P}$. The compressibility at

$P=0$ is 49.5×10^{-6} per megabar, and at 1000 megabars it is 34.4×10^{-6} per megabar. The freezing pressure and volume change were also determined at a few temperatures, and the following results obtained:

Temp.	Freezing pressure. Megabars.	$(V_2 - V_s \text{ c.c.})$	dP/dT .
13.9	1	0.054	68
21.9	570	0.050	71
29.6	1110	—	—
31.4	1210	0.047	74
38.9	1800	0.042	77

The latent heat of fusion per gram is found to be 25 cal.

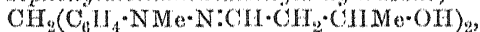
J. F. S.

The Liquid Crystals of Agaricic Acid. PAUL GAUBERT (*Compt. rend.*, 1919, 168, 277—279).—Agaricic acid gives two types of liquid crystals, one belonging to the cubic system and the other being optically uniaxial and positive. The crystals are but slightly birefringent, and consequently the polychroism is feeble.

W. G.

Phytochemical Reductions. XV. The Conversion of Acetaldo into Optically Active β -Butylene Glycol by Yeast. CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, 92, 96—110).—The reaction, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CHO} \rightarrow \text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, takes place in the presence of yeast both when actively fermenting sugar and when, also, sugar is not added. A dextrorotatory product was obtained. The β -butylene glycol was, amongst other methods, characterised by preparing the di- α -naphthylurethane derivative, m. p. 154° , by its treatment with α -naphthylcarbimide.

A method is given for preparing in good yield acetaldo by the action of disodium sulphite on aldehyde in the cold (at -15°). From the aldol were prepared the β -bromophenylhydrazone, $\text{C}_{10}\text{H}_{13}\text{ON}_2\text{Br}$, white, seemingly hexagonal leaflets, m. p. 127 — 128° , and also the diphenylmethanedimethylidihydrazone,



colourless plates, m. p. 117° .

S. B. S.

Phytochemical Reductions. XVI. The Conversion of Citral into Geraniol by Yeast. CARL NEUBERG and (MME.) ELISABETH KERB (*Biochem. Zeitsch.*, 1918, 92, 111—123).—This reaction takes place both in the presence and absence of added sugar. The geraniol which is produced is accompanied by some optically active substance which has not yet been identified. The authors describe the two following derivatives of cyclocitral: the thiosemicarbazone, $\text{C}_{11}\text{H}_{19}\text{N}_3\text{S}$, white leaflets, m. p. 200 — 201° , and the p-nitrophenylhydrazone, $\text{C}_{16}\text{H}_{21}\text{O}_2\text{N}_3$, orange crystals, m. p. 125° .

S. B. S.

Preparation of Soluble Starch. A. LEULIER (*J. Pharm. Chim.*, 1918, [vii], **18**, 291).—Twenty-five grams of starch are boiled for fifteen minutes under a reflux apparatus with a mixture of 100 grams of 95% alcohol and 5 grams of sulphuric acid; the starch is then collected on a filter and washed with water or alcohol until free from acidity. Starch thus treated is insoluble in cold water, but very soluble in hot water. [See, further, *J. Soc. Chem. Ind.*, 1919, 86A.] W. P. S.

The Preparation of Methylamine from Chloropicrin. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (*T.*, 1919, **115**, 159—162).

The Present Condition of the Benzene Problem. HERMANN PAULY (*J. pr. Chem.*, 1918, [ii], **98**, 106—135).—The various representations suggested for the benzene molecule are discussed. From a consideration of the relationships between the physical constants of benzene derivatives, the corresponding hydrogenated compounds, etc., the following conclusions are drawn: (1) The atoms of the benzene molecule lie in one plane. (2) The benzene ring must be symmetrically arranged and the linkings uniform. (3) Neither centric nor olefinic linkings are present, the degree of saturation of the linkings being approximately midway between those of simple and double linkings. Thiele's formula, the valence-electronic representation of benzene, the tetrahedral model, and the problem of orientation are also considered. T. H. P.

II-10-Bromophenanthrene-3- or -6-sulphonic Acid. HÅKAN SANDQVIST (*Annalen*, 1918, **417**, 1—16).—A hot aqueous solution of potassium phenanthrene-3-sulphonate is cooled to about 50° until crystals begin to separate, and a solution of bromine in water saturated at the ordinary temperature (about 3 mols. of bromine) is added gradually, whereby is obtained, in addition to oxidation products, potassium II-10-bromophenanthrene-3- or -6-sulphonate. The crude salt is converted through the chloride into II-10-bromophenanthrene-3- or -6-sulphonic acid, $C_{14}H_8Br \cdot SO_3H \cdot 4H_2O$, an almost white, non-crystalline mass, m. p. 152—153°, or, anhydrous, 223° (in a closed capillary, m. p. 160—170°), which has an astringent but, unlike the I-isomeride (*A.*, 1917, i, 552), no sweet taste, forms yellow, flocculent solutions, and shows some tendency to form liquid crystals. The potassium, ammonium, sodium, calcium, barium, and copper salts are described. The methyl ester, flattened needles, has m. p. 158°, the ethyl ester, needles, has m. p. usually 143.5°, but sometimes 134° (to a turbid liquid); the former yields methyl phenanthraquinone-3-sulphonate by oxidation with chromic and acetic acids. II-10-Bromophenanthrene-3- or -6-sulphonyl chloride, prepared from the potassium salt, forms faintly yellow prisms, m. p. 199—199.5°, from which are prepared the amide, $C_{14}H_{10}O_2NBrS$, needles, m. p. 266.5°, and the anilide, needles or leaflets, m. p. 211°. C. S.

I-10-Chlorophenanthrene-3- or -6-sulphonic Acid and 10-Chlorophenanthrene. HÅKAN SANDQVIST (*Annalen*, 1918, 417, 17—33).—It has been shown (A., 1917, i, 552) that the abnormal viscosity and anisotropy of solutions of I-10-bromophenanthrene-3- or -6-sulphonic acid disappear when the bromine is replaced by the $\cdot\text{SO}_3\text{H}$ or $\cdot\text{C}_{14}\text{H}_7\text{Br}\cdot\text{SO}_3\text{Me}$ group. It is now found that they are increased when the bromine is replaced by a chlorine atom.

I-10-Chlorophenanthrene-3- or -6-sulphonic acid, prepared by fusing together I-10-bromophenanthrene-3- or -6-sulphonyl chloride and phosphorus pentachloride, and heating the resulting chloride with water at about 145° , forms a white, microcrystalline powder possessing an acid, sweet, astringent taste. A 0.04*N*-solution has a viscosity 1.03 at 18° (water at $18^\circ=1$); this is increased to about 140 by the addition of one-sixth volume of 3*N*-hydrochloric acid, the value for I-10-bromophenanthrene-3- or -6-sulphonic acid being increased only to about 6 by similar treatment. The air-dried acid, m. p. $160\text{--}161^\circ$, contains $3\text{H}_2\text{O}$ (decomp.); the anhydrous acid has m. p. $206\text{--}207^\circ$. The ammonium, sodium, potassium, calcium, barium, and copper salts are described. The methyl ester, leaflets or prisms, has m. p. $172\text{--}172.5^\circ$, and the ethyl ester, colourless crystals, m. p. $182.5\text{--}183^\circ$. The chloride, $\text{C}_{14}\text{H}_8\text{Cl}\cdot\text{SO}_2\text{Cl}$, prepared as above, forms prisms, m. p. $196\text{--}197^\circ$, and from it have been obtained the amide, needles, m. p. $281\text{--}282^\circ$, and anilide, crystals, m. p. $197\text{--}198^\circ$.

10-Chlorophenanthrene, $\text{C}_{14}\text{H}_9\text{Cl}$, m. p. $35\text{--}55^\circ$ (purest specimen, $52.5\text{--}53.5^\circ$), b. p. $343\text{--}346^\circ$, is obtained, together with other products (of which 9:10-dichloroanthracene and 9:10-phenanthrene dichloride have been identified), by adding a cold solution of chlorine (26 grams) in carbon disulphide to phenanthrene (50 grams) dissolved in the same solvent. It yields phenanthraquinone by oxidation, forms a *picrate*, $\text{C}_{14}\text{H}_9\text{Cl}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3\cdot\text{OH}$, yellowish-red needles, m. p. $111\text{--}112^\circ$, and is converted by sulphonation at $165\text{--}170^\circ$ into a sulphonic acid, from which the preceding I-10-chlorophenanthrene-3- or -6-sulphonyl chloride, m. p. $196\text{--}197^\circ$, can be prepared.

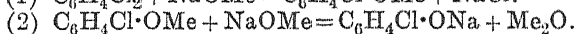
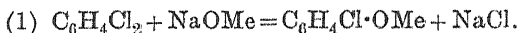
C. S.

The Mobility of the Methylnitroamino-group in the Derivatives of Tetranitrophenylmethylnitroamine and in Trinitrodi(methylnitroamino)benzene. C. F. VAN DUIN (*Rec. trav. chim.*, 1919, 38, 89—100).—A study of the action of ammonia, aniline, and *m*-nitroaniline on certain derivatives of 2:3:4:6-tetranitrophenylmethylnitroamine obtained by substituting the nitro-group in position 3 by an hydroxyl, an anilino-, a methylnitroamino-, an amino-, and a dimethylamino-group. The results show that a negative substituent in this position hinders the substitution of the methylnitroamino-group, whilst a positive substituent increases its mobility. As opposed to this, however, is the fact that in 2:4:6-trinitro-3-dimethylaminophenyl-

methylnitroamine, the methylnitroamino-group is not replaced by *m*-nitroaniline.

In the action of ammonia on 2:4:6-trinitro-1:3-di(methylnitroamino)benzene, two *compounds*, one having m. p. 195—196° (corr.) and the other having m. p. 144° (corr.), were obtained, but could not be characterised. W. G.

The Formation of Phenol in the Action of Sodium Methoxide on the Higher Chlorobenzenes. P. W. DE LANGE (*Rec. trav. chim.*, 1919, **38**, 101—105. Compare Holleman and Mooy, A., 1916, i, 22).—The author finds that *p*-chloroanisole and *p*-dichlorobenzene when heated in sealed tubes at 176—177° with sodium methoxide in methyl alcohol each yielded *p*-chlorophenol and methyl ether, the reaction being far more complete with the *p*-chloroanisole than with the dichlorobenzene. He considers that the reaction with dichlorobenzene takes place in two stages, as follows:



W. G.

Velocity of Nitration of Phenols in Ethereal Solution. II. ALFONS KLEMENC and ELISABETH EKL (*Monatsh.*, 1918, **39**, 641—696. Compare A., 1914, i, 272).—The velocity constants of the nitration of phenol, guaiacol, *o*- and *p*-cresol, and resorcinol methyl ether have been determined. Nitration is, in general, found to be a positive autocatalytic process, and the rate of nitration is dependent on the proportion of nitrogen peroxide or nitrous acid in the nitric acid. From this point of view, a mathematical expression for the velocity of nitration of a benzene derivative has been developed which, when applied to the particular case of phenols, takes into account the fact that the nitrous acid formed during the course of nitration (the cause of the autocatalytic nature of the process) is itself absorbed by the phenol.

Pure nitric acid, free from nitrogen peroxide and nitrous acid, does not cause nitration. Nitrogen peroxide induces both the nitrating and oxidising action of nitric acid towards derivatives of benzene.

In the case of nitration in ethereal solution, action either does not occur at all or rapidly comes to an end if the number of molecules of nitric acid is greater than that of the phenol or guaiacol, this behaviour being, apparently, opposed to the law of mass action.

The necessary solutions are obtained by dissolving anhydrous nitric acid in dry ether at a temperature of −80° (solutions prepared in this manner remain colourless at 0° for weeks), and by dissolving nitrogen peroxide in the same solvent in a special form of apparatus, which is figured in the text and allows the necessary adjustment of concentration and removal of known amounts of solution. The course of the reaction is followed by

determining the decrease in the titre of the nitric acid at given intervals. In the case of phenol, this can be done directly with standard barium hydroxide solution (the nitrophenol behaving as indicator) during the early stages of the reaction; during the later stages, the end-point is obscured by coloured bye-products, and it is then preferable to shake the ethereal solution with saturated potassium chloride solution and to add potassium hydroxide or barium hydroxide until the nitric acid is neutralised, when the next drop extracts a portion of the nitrophenol from the ether and colours the aqueous solution deep red. In the cases of guaiacol and other phenols, this method cannot be used, and recourse must be had to the iodometric process previously described (*loc. cit.*).

In addition to the phenols already mentioned, experiments with catechol, resorcinol, and quinol are also described. In the first two cases, satisfactory results could not be obtained; with quinol, the initial reaction consisted in the evolution of nitric oxide and formation of quinhydrone, which gradually underwent nitration. It is noteworthy that the presence of nitrogen peroxide is here found to be essential to the oxidising action of the nitric acid.

H. W.

Oxidation of Quinol and its Sulphonic Acids by means of Fehling's Solution. JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], 98, 81—95. Compare A., 1911, i, 339).—Further experiments show that, when oxidised by Fehling's solution in absence of air, quinol and its sulphonic acids require almost exactly 3 atoms of oxygen per molecule, and give dihydroxyquinol or its sulphonic acids. The less amount of Fehling's solution earlier found sufficient with low concentrations of quinol (compare Bourquelot and Fichtenholz, A., 1910, i, 273) is explained by concurrent oxidation at the expense of atmospheric oxygen. In presence of sulphite, quinol and its sulphonic acids are oxidised by means of Fehling's solution principally to dihydroxyquinoldisulphonic acid, 5 or 4 atoms, respectively, of oxygen being used; this oxidation proceeds by way of quinone, quinolsulphonic acid, quinonesulphonic acid, and quinoldisulphonic acid, and not by way of dihydroxyquinone and its sulphonic acids. Unlike quinone and its sulphonic acids, dihydroxyquinone and its sulphonic acids do not unite with sulphite. Part of the quinol, which is not oxidised by Fehling's solution to the readily separable dihydroxyquinonedisulphonate, yields a readily soluble, pale-coloured isomeride, but the most important side reaction is the action of the alkali on the quinone-sulphonate, which should lead through hydroxyquinolsulphonate to the final product of oxidation, hydroxyquinonesulphonate.

T. H. P.

Some Derivatives of Resorcinol. H. VERMEULEN (*Rec. trav. chim.*, 1919, 38, 106—111).—2-Nitroresorcinol when added to nitric acid (D 1.5) in the cold yields 2:4-dinitroresorcinol, m. p. 146°, which when converted into its potassium salt and heated with an excess of methyl sulphate gives 2:4-dinitro-1:3-dimethoxy-

benzene; this, when reduced with tin and hydrochloric acid in alcoholic solution and the product treated with acetic anhydride, gives 2-nitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 161–162°. This compound on nitration yields 2:6-dinitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 129°, which when hydrolysed gives 2:6-dinitro-4-amino-1:3-dimethoxybenzene, m. p. 141°. 4-Acetyl-amino-1:3-dimethoxybenzene, m. p. 117°, when nitrated in acetic acid solution yields 6-nitro-4-acetyl-amino-1:3-dimethoxybenzene, m. p. 173°, which is also obtained by the acetylation of 6-nitro-4-amino-1:3-dimethoxybenzene, m. p. 136–137°, obtained by the reduction of 4:6-dinitro-1:3-dimethoxybenzene. W. G.

Acetylsalicylic [*o*-Acetoxybenzoic] Acid. HENRY L. DAHM (*J. Ind. Eng. Chem.*, 1919, **11**, 29–30).—The melting point of aspirin is determined by immersion of the capillary tube in a stirred paraffin oil bath heated at the rate of 1° per minute, the thermometer being immersed during the whole time of heating, but the melting-point tube inserted only when the temperature reaches 130°. The free salicylic acid present may be determined by comparison of the colour given with dilute ferric chloride with a series of cobalt chloride solutions of various concentrations. [See *J. Soc. Chem. Ind.*, 1919.] T. H. P.

The Elimination of the Carbethoxyl Group from Tautomeric Systems. I. Derivatives of Indene. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (*T.*, 1919, **115**, 143–159).

Preparation of Mercury Derivatives of Phthaleins and Analogous Compounds. SACCHARINFABRIK AKT.-GES. VORM. FAHLBERG, LIST, & Co. (D.R.-P. 308335; from *Chem. Zentr.*, 1918, ii, 881–882).—Neutral solutions of the alkali salts of phthaleins, succineins, and “sacchareins” are boiled with a large excess of a mercuric salt, particularly mercuric chloride, whereby uniform products are formed in an easily isolable condition. Thus, fluorescein and mercuric chloride yield a reddish-brown product, insoluble or sparingly soluble in the usual organic media, soluble in sodium carbonate, sodium hydroxide, or ammonia, to deep red solutions, which show a strong, greenish-yellow fluorescence when diluted. The ammoniacal solution is blackened by ammonium sulphide at its boiling point. The sodium salt of methylfluorescein gives a pale brown derivative with mercuric chloride which dyes silk orange-yellow. Mercuriated compounds from dibromofluorescein, tetrabromofluorescein, tetraiodofluorescein, phenolphthalein, tetraiodophenolphthalein, quinolphthalein, hydroxyquinolphthalein, resorcinsuccinein, cresorcinsuccinein, and resorcinsaccharein are also described. H. W.

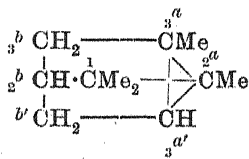
The Reduction of Aromatic Ketones. W. D. COHEN (*Rec. trav. chim.*, 1919, **38**, 72–88).—In acid solution, benzophenone is reduced with the formation of benzopinacol, benzhydrol not being formed. If the action is energetic, a little diphenylmethane is

formed. In an alkaline medium, on the other hand, benzhydrol is almost exclusively obtained unless the alkali is very weak, in which case a little benzopinacone is formed. An energetic reduction produces some diphenylmethane. In neutral medium, as when reduced by aluminium amalgam in alcohol, benzophenone yields 68% of benzhydrol and 32% of benzopinacone. W. G.

Preparation of β -Anthrimides. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 308666; from *Chem. Zentr.*, 1918, ii, 882).—The products of the action of ammonia on β -diazanthraquinones are heated in solvents of high boiling point with or without a condensing agent. Thus, anthraquinone- β -diazonium sulphate is made into a paste with alcohol and treated with well-cooled, concentrated alcoholic ammonia; the product is heated with nitrobenzene under reflux, when $\beta\beta'$ -dianthrimide separates as a dark brownish-red substance, which becomes yellowish-brown when dried or acidified; it forms a scarlet solution in concentrated sulphuric acid, which gradually becomes olive and then green. The product from 1:3-dibromoanthraquinone- β -diazonium sulphate and alcoholic ammonia gives *tetrabromo- β -dianthrimide* (partly as the benzoyl derivative, which is hydrolysed with concentrated sulphuric acid) when heated to gentle boiling with nitrobenzene and benzoyl chloride. The substance is yellow and yields a bluish-green solution in concentrated sulphuric acid; it dyes cotton yellow from a reddish-brown bath. *Dichlorobisdiazanthraquinoneamide* (from diazotised 1-chloro-2-aminoanthraquinone and ammonia in excess) is pale yellow, and is converted by treatment with boiling nitrobenzene and benzoyl chloride into 1:1'-*dichloro-2:2'-dianthrimide*, orange-yellow, matted needles soluble in concentrated sulphuric acid to a pure blue solution; it dyes cotton orange-yellow from a reddish-brown bath. H. W.

***sec.*- β -Methylcamphor and *sec.*- β -Phenylcamphor, a New Series of Synthetic Camphors, and *tert.*-Naphthylborneol and Naphthylcamphene.** J. BREDT (*J. pr. Chem.*, 1918, [ii], 98, 96—105).—In consequence of the publication of Ruzicka's paper (*A.*, 1918, i, 398), the author gives a short account of work carried out in 1914—1918.

[With MARIA SAVELSBERG.]—The action of magnesium methyl iodide on camphor or on fenchone yields the tertiary alcohols, methylborneol and methylfenchol, which, under the action of dehydrating agents, yield one and the same hydrocarbon, $C_{11}H_{18}$, b. p. 172—175°, m. p. 71—73°, which shows great stability towards permanganate, and is regarded as a homocyclene of the annexed structure. When treated with acetic and sulphuric acids, the hydrocarbon yields an *acetyl* compound, $C_{13}H_{22}O_2$, b. p. 106—107°/13 mm., and this on hydrolysis gives a secondary *alcohol*, $C_{11}H_{20}O$, m. p. 193°, which forms a *phenylurethane*, m. p. 102°; oxidation of the alcohol yields a



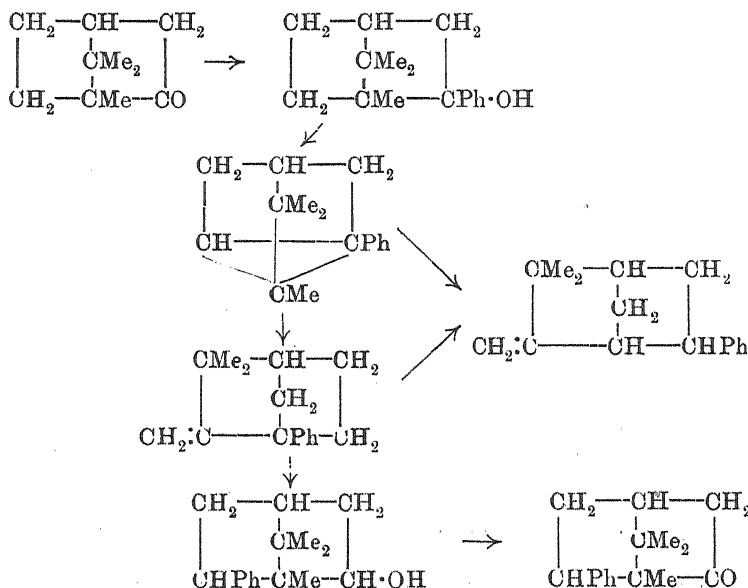
ketone (β -methylcamphor), $C_{11}H_{18}O$, m. p. 167–168°, giving an *oxime*, m. p. 125–127°, and a *semicarbazone*, m. p. 255° (decomp.), and yielding 2-methylcamphoric acid, $C_{11}H_{18}O_4$, m. p. 191°; the *anhydride* of the acid has m. p. 205.5–207°. The properties of these products indicate that they belong to the camphor series, so that, in the splitting of the trimethylene ring of the hydrocarbon (see formula above), the linking $3^a-3^a'$ is ruptured. This indication is confirmed by the molecular refraction of the *ethyl* ester of the acid; this ester has D_4^{25} 1.0289, which differs but little from the value, D_4^{25} 1.0298, for ethyl camphorate, whereas ethyl *isofencho*-camphorate has D_4^{25} 1.0054. The specific exaltation of the molecular refraction of the ester of the new acid, $R\Sigma_D = -0.229$, is similar to that, -0.18 , for ethyl camphorate, and is conditioned by the annexed grouping, whilst in ethyl *isofencho*-

camphorate the grouping $\begin{array}{c} \text{CH}-\text{CH}_2-\text{C}-\text{Me} \\ | \quad | \\ \text{Me} \end{array}$ produces no exaltation. The following further derivatives of the 2-methylcamphoric acid were prepared: the *dichloride*, b. p. 155°/15 mm., the *chlorinated chloride*, the *chloro-anhydride*, m. p. 204–206°, the *sec.-tert.-amino-acid*, m. p. 162–163°, and its *calcium salt*, and the *acid imide*, m. p. 256°.

[With A. C. HEINEMANN and F. GOBLT.]—The interaction of magnesium phenyl bromide and camphor, followed by treatment of the product with water and dilute hydrochloric acid, yields the *tert*-phenylborneol, m. p. 41°, b. p. 119.5–120.5°/2–2.5 mm., $[\alpha]_D^{20} -50.33^\circ$ (in benzene), already prepared by Haller. Treatment of this tertiary alcohol with acetic anhydride gives a liquid *hydrocarbon*, $C_{16}H_{26}$, b. p. 99°/2 mm., D_4^{25} 0.9920, $[\alpha]_D^{19} +3.27^\circ$, which is converted into the *acetyl* derivative of a tertiary alcohol, b. p. 136°/2 mm., m. p. 87°. This hydrocarbon partly undergoes rearrangement to an *isomeride*, b. p. 86°/2 mm., D_4^{27} 1.0034, $[\alpha]_D^{18} -3.75^\circ$, whilst a third *isomeride*, b. p. 106°/2 mm., m. p. 33–34.5°, $D_4^{29.6}$ 0.9742, is formed in good yield on repeated dry distillation of the above acetyl compound. The hydrocarbon, b. p. 99°/2 mm., does not combine with hydrogen chloride in light petroleum solution, but the isomeride, b. p. 86°, forms the *hydrochloride*, $C_{16}H_{24}Cl$, m. p. 76.5°, which with milk of lime gives a *tertiary alcohol*, $C_{16}H_{22}O$, b. p. 106.5°, $[\alpha]_D^{40} +23.06^\circ$, isomeric with the *tert*-phenylborneol. Hydrolysis of the above acetyl derivative yields a secondary *alcohol*, $C_{16}H_{22}O$, m. p. 115–116°, which, like the products derived from it, is optically inactive. Oxidation of this alcohol by means of chromic acid gives a *phenylcamphor*, $C_{16}H_{20}O$, m. p. 68°, the formation of which takes place as shown on p. i, 127.

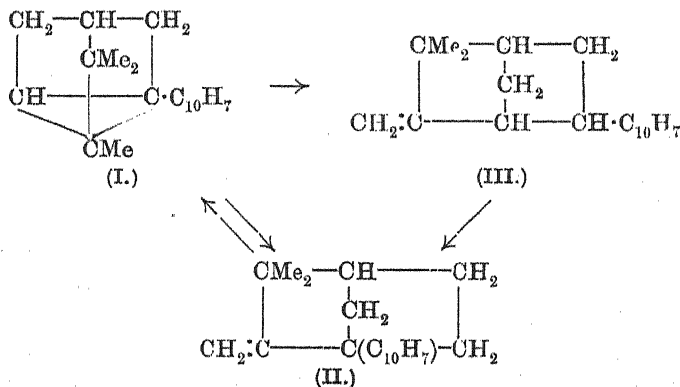
The new phenylcamphor forms a *semicarbazone*, m. p. 189–190°, and an *oxime*, m. p. 141–142.5°, and when reduced with sodium and alcohol gives a mixture of phenylborneol and phenylisoborneol, which were not separated. With sodiopotassamide and amyl nitrite, phenylcamphor yields the *isonitroso*-derivative, which forms

greenish-white crystals, m. p. 189°, and this with sodium hydrogen sulphite gives *phenylcamphorquinone*, a golden-yellow substance, m. p. 145°. The latter is also obtained by the action of permanganate on *phenylcamphorcarboxylic acid*, m. p. 149–150° (evolu-



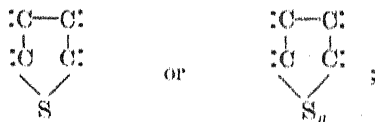
tion of CO_2), which is formed from phenylcamphor with the help of sodiopotassamide and carbon dioxide. *Phenylcamphoric acid*, $\text{C}_{16}\text{H}_{20}\text{O}_4$, m. p. 123·5°, is formed by the protracted action of permanganate solution on the quinone; its *anhydride*, $\text{C}_{16}\text{H}_{18}\text{O}$, m. p. 173·5°, was prepared.

[With H. DUSSIER.]—The action of magnesium α -naphthyl bromide on camphor yields *tert.-naphthylborneol*, m. p. 122–124°,

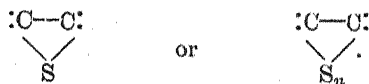


$[\alpha]_D^{15} -41.96^\circ$ in benzene. When subjected to dry distillation, this alcohol yields the *naphthylcamphene*, $C_{20}H_{22}$, which crystallises in felted needles, m. p. $92-93^\circ$, b. p. $210^\circ/16$ mm., and gives no hydrochloride with dry hydrogen chloride in ethereal solution. Treatment of the hydrocarbon with acetic and sulphuric acids yields only an *isomeride*, m. p. $116-117^\circ$. From results obtained with methylcyclohexene and phenylcamphene, it may be assumed that the naphthylcamphene, m. p. $92-93^\circ$, has structure I or II, and that treatment with acetic and sulphuric acids, under the influence of the naphthyl residue, leads to rearrangement to the compound III, which cannot be acetylated. T. H. P.

Condensation of Unsaturated Compounds in Relation to Terpenes, Resins, and Caoutchouc. H. J. PRINS (*Chem. Weekblad*, 1919, **16**, 64-74).—The type of condensation discussed is that between molecules of the same substance containing the group $C=C$. The reaction is brought about by catalysts, such as acids, acid anhydrides, halogens and halogen compounds with active halogen, sulphur and sulphur compounds (persulphides), oxygen and peroxides, metallic oxides, and metals. The catalyst and substrate are "reciprocally activated." Three reactions are possible: polymerisation of the unsaturated substance, combination of catalyst with the substance at the double bond, and combination of catalyst with the polymerised substance formed. The theory of reciprocal activation is discussed in relation to the simultaneous polymerisation and oxidation of unsaturated hydrocarbons, such as terpenes, the formation of resins, and the vulcanisation of caoutchouc. The following theory for the last-mentioned process is suggested. The caoutchouc molecule is rendered active by means of the catalyst sulphur, whilst the sulphur undergoes a change analogous to the formation of ozone from oxygen in presence of unsaturated substances. There results (1) a simple polymerisation of the caoutchouc molecule with formation of *cyclobutane* derivatives; (2) polymerisation of the caoutchouc molecule with inclusion of sulphur in the ring, giving compounds of the type



(3) direct addition of sulphur at the double bond to form :



W. S. M.

Constituents of Resins. III. Further Investigation of Sialesinol from Siamese Gum Benzoin. ALLOIS ZINKE and HANS LIEB (*Monatsh.*, 1918, **39**, 627-639).—It has been previously shown that the benzoresinol obtained by Lüdy from

Sumatra gum benzoin (A., 1893, i, 480—666) is probably a mixture of *d*-sumaresinol and *l*-benzoresinol (A., 1918, i, 502); further examination of the substance prepared according to Lüdy's directions only led to the isolation of siaresinol (A., 1918, i, 398). Lüdy's benzoresinol should therefore be deleted from the literature.

Further examination of *d*-sumaresinol and siaresinol has shown that these substances are acidic in character, and that the acidic hydrogen is contained in the carboxyl, and not in the hydroxyl group as assumed by Lüdy (*loc. cit.*); the former is therefore to be regarded as *d*-sumaresinolic acid and the latter as *d*-siaresinolic acid. Oxidation of *d*-siaresinolic acid leads to the formation of a monobasic acid, $C_{27}H_{40}O_4$, and the loss of three atoms of carbon and eight atoms of hydrogen appears to denote the elimination of a propyl or an isopropyl group; the formula for the parent substance may be written $C_3H_7 \cdot C_{26}H_{40}O_2 \cdot CO_2H$.

[With LUDWIG ZECHNER.]—*Silver siaresinolate* forms a white powder which darkens in colour when preserved, and decomposes when warmed with water, acetone, or alcohol. It is converted by methyl iodide into *methyl siaresinolate*, which crystallises in prismatic crystals with $1.5H_2O$ from aqueous alcohol, m. p. about 150° , in needles with $\frac{1}{2}H_2O$ from benzene, and in anhydrous, prismatic crystals, m. p. 169 — 170° , from light petroleum. The *ethyl* ester separates from light petroleum in needles or prismatic platelets, m. p. 108° ; from aqueous alcohol in nodular masses, which melt indefinitely at 102° and contain water of crystallisation. The mixed *anhydride* of acetic and siaresinolic acids melts at 125 — 127° after softening at 104° .

Chromic acid oxidises the double compound of acetic and *d*-siaresinolic acid to an acid, $C_{27}H_{40}O_4$, short prisms, m. p. 317° , $[\alpha]_D^{25} -193.8^\circ$ in chloroform solution; the *potassium* salt, long, white needles with $3\frac{1}{2}H_2O$, and the *methyl* ester, colourless leaflets, m. p. 186 — 187° , are described. H. W.

Hydroxymethylfurfuraldehyde. J. A. MIDDENDORP (*Rec. trav. chim.*, 1919, 38, 1—71).—The author finds that ω -hydroxymethylfurfuraldehyde, obtained by the action of acids on the hexoses, can be distilled unchanged in an absolute vacuum, giving a distillate, b. p. 114 — $116^\circ/1$ mm., which will crystallise and has m. p. 31.5° , $D_4^{25} 1.268$, $D_4^{36} 1.2629$, $n_D^{36} 1.556$, $n_D^{34} 1.552$, $n_D^{33} 1.563$, and its heat of combustion is 664.8 cal. per gram-mol. Contrary to the general statements, the author finds that this aldehyde is miscible with water in all proportions, and that there is no indication of the formation of a hydrate. It gives a *phenylmethylhydrazone*, m. p. 161° , and an *aldazine*, m. p. 168° (decomp.), and its hydroxyl group may readily be replaced by halogen by the action of the hydrogen halide in dry ether. ω -Chloromethylfurfuraldehyde is readily converted into ω -methoxymethylfurfuraldehyde, an oil, b. p. 68 — $70^\circ/2$ mm., $D_4^{17.9} 1.146$, $n_D^{19.6} 1.5088$ giving a *phenylhydrazone*, m. p. 56 — 57° , a *p*-nitrophenylhydr-

azone, m. p. 140—141°, an *oxime*, an *aldazine*, m. p. 86°, a *semicarbazone*, m. p. 170°, and a *semioxamazone*, m. p. 209—210°. Similarly, ω -ethoxymethylfurfuraldehyde gives a *p*-nitrophenylhydrazone, m. p. 140—141°, an *oxime*, an *aldazine*, m. p. 70°, and a *semioxamazone*, m. p. 212—213°. Benzoyloxymethylfurfuraldehyde gives a phenylhydrazone, m. p. 112°, a *p*-nitrophenylhydrazone, m. p. 142°, an *oxime*, m. p. 85—85.5°, an *aldazine*, m. p. 163°, a *semicarbazone*, m. p. 198°, and a *semioxamazone*, m. p. 204° (decomp.).

When distilled at a pressure of 10—20 mm., hydroxymethylfurfuraldehyde is partly decomposed, giving its anhydride, difurfurylmethyl ether, which yields a *semicarbazone*, m. p. 255°, and when oxidised by moist silver oxide gives di(2-methyl-5-carboxyfuryl) ether, m. p. 165°.

Sodium hydroxide readily decomposes hydroxymethylfurfuraldehyde, giving 2:5-dihydroxymethylfuran, m. p. 80°, and 5-hydroxymethylpyromucic acid. Under similar conditions, methoxymethylfurfuraldehyde gives 2-hydroxymethyl-5-methoxymethylfuran, b. p. 132—134°/23 mm., m. p. 37°, $n_D^{16.5}$ 1.4860, and 5-methoxymethylpyromucic acid, m. p. 66—66.5°; the ethoxy-aldehyde similarly gives 2-hydroxymethyl-5-ethoxymethylfuran, b. p. 152—157°/20 mm., n_D^{15} 1.4865, and 5-ethoxymethylpyromucic acid, m. p. 62°.

Hydroxymethylfurfuraldehyde condenses with ethyl malonate, giving *ethyl hydroxymethylfurfurylidenemalonate*, m. p. 48.5°, b. p. 221°/11 mm., D_4^{20} 1.1648, n_D^{20} 1.539, n_D^{25} 1.536, and with malonic acid, giving *hydroxymethylfurfurylidenemalonic acid*, decomposing at 130°.

Ammonia or potassium cyanide react readily in alcoholic solution with hydroxy-, methoxy-, or ethoxy-methylfurfuraldehyde, but the products in every case resinify.

From a study of the absorption spectra of the coloured products obtained from furfuraldehyde and its methyl and hydroxymethyl derivatives, respectively, with the following reagents, resorcinol, Sesamé oil, β -naphthol, acetone, diphenylamine, egg-albumin, aniline acetate, narcotine, and orcinol, it is shown that the coloured products formed by warming sucrose with hydrochloric acid and the respective reagents resemble those obtained from hydroxymethylfurfuraldehyde, but differ from those obtained from furfuraldehyde itself. It is shown that diphenylamine is the most satisfactory reagent for distinguishing between pentoses and hexoses, and that the reaction with acetone is the most satisfactory for distinguishing methylpentoses from pentoses and hexoses. W. G.

The Alkaloids of *Holarrhena congolensis*. FRANK LEE PYMAN (T., 1919, 115, 163—166).

Nicotine Content of the Smoke of Heavy, Light, and "Nicotine-free" Cigars. W. STORM VAN LEEUWEN (*Arch. exp. Path. Pharm.*, 1918, 84, 282—316).—This content was measured

physiologically by the effect on the blood-pressure of an acid extract of the smoke, and bears no relationship to the trade description or even to the nicotine content of the cigars themselves. The smoke of so-called nicotine-free cigars (Wendt) contains as much as that of average normal ones. A full account of earlier work is given.

G. B.

Cyclic Acetone Bases. C. HARRIES (*Annalen*, 1918, 417, 107—191. Compare A., 1896, i, 317).—The author has shown that vinylidiacetonamineoxime (4-oximino-2:2:6-trimethylpiperidine) yields α -4-amino-2:2:6-trimethylpiperidine by reduction with zinc dust and cold alcoholic hydrochloric acid, and β -4-amino-2:2:6-trimethylpiperidine by reduction with sodium and boiling amyl alcohol (*loc. cit.*, and A., 1897, i, 293). These two bases behave differently towards carbon disulphide. Whilst the β -base yields only one dithiocarbamate which cannot be converted into a thiocarbimide by mercuric chloride, the α -base yields an easily soluble dithiocarbamate, which is changed by boiling water into a sparingly soluble dithiocarbamate; from the last, hot aqueous mercuric chloride solution produces a substance which has the composition of the expected thiocarbimide, but not its properties, and is therefore probably an internal thiocarbamide. By treatment with iodine, the two α -dithiocarbamates (2 mols.) lose carbon disulphide (1 mol.) and hydrogen sulphide (1 mol.) and yield two isomeric thiocarbamides, probably having the constitution



these are probably syn- and anti-stereoisomerides, and so also are the two α -dithiocarbamates.

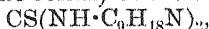
The question why the β -base does not yield an analogous series of isomerides cannot be answered at present.

[With A. BAUDREXEL, H. HOHENEMSER, and R. HAARMANN.]—Between 1896 and 1908, the reduction of 4-oximino-2:2:6-trimethylpiperidine to α -4-amino-2:2:6-trimethylpiperidine by cold alcoholic hydrogen chloride and zinc dust has frequently been effected. It is all the more remarkable, therefore, that the authors, using present-day zinc dust (since 1913), have obtained, not the above α -base, but 2:2:6-trimethyl-4-piperidone. In order to prepare the α -base, therefore, 4-oximino-2:2:6-trimethylpiperidine has been reduced by 3% sodium amalgam in 80% alcoholic solution at 10—20°, 25% hydrochloric acid being constantly added to maintain an acid reaction. This method produces about equal weights of α - and β -4-amino-2:2:6-trimethylpiperidine; the hydrochloride of the latter is insoluble in absolute alcohol.

[With BERNHARD SCHELLHORN.]—Whether reduced by cold alcoholic hydrochloric acid and zinc dust or by boiling amyl alcohol and sodium, 4-oximino-2:2:6:6-tetramethylpiperidine yields only one 4-amino-2:2:6:6-tetramethylpiperidine, leaflets, m. p. 16—18°, b. p. 79°/7 mm., which is converted by acetic anhydride into the acetate of the acetyl-amino-derivative, m. p. 205°; the acetyl-amino-

derivative itself, $C_{11}H_{22}ON_2$, forms pyramidal crystals, m. p. 120° , b. p. $161-163^\circ/6-8$ mm.

In cold ethereal solution, 4-amino-2:2:6:6-tetramethylpiperidine (2 mols.) and carbon disulphide (1 mol.) yield 4-amino-2:2:6:6-tetramethylpiperidine 2:2:6:6-tetramethylpiperidylthiocarbamate, $C_9H_{18}N \cdot NH \cdot CS \cdot SH, C_9H_{18}N \cdot NH_2$, crystals, m. p. 154° , but in the ratio of 1:1 yield tetramethylpiperidylthiocarbamic acid, $C_9H_{18}N \cdot NH \cdot CS \cdot SH$, m. p. 180° ; this, and also the preceding salt, are converted into a substance, m. p. 205° (decomp.), by recrystallisation from boiling water. The dithiocarbamic acid in boiling aqueous-alcoholic solution is converted by alcoholic iodine into the hydriodide (two crystalline forms) of the thiocarbamide,



triangular plates, m. p. 170° .

Corresponding with the production of two alkamines by the reduction of 2:2:6-trimethyl-4-piperidone (Harries, A., 1897, i, 293), it is found that 2:2-dimethyl-6-isobutyl-4-piperidone, reduced by sodium amalgam in faintly acid solution, yields a mixture of labile *cis-valerdiacetonalalkamine* [4-hydroxy-2:2-dimethyl-6-isobutylpiperidine], $NH < \begin{array}{c} CH(CH_2Pr^a) \cdot CH_2 \\ CMe_2 \quad \quad \quad CH_2 \end{array} > CH \cdot OH$, m. p. $91-92^\circ$ (hydrochloride, m. p. 215°), and the stable *trans-isomeride*, m. p. 65° ; the former is converted into the latter by heating with a solution of sodium amyl oxide.

2:2-Dimethyl-6-isobutyl-4-piperidone forms an *oxime*, $C_{11}H_{22}ON_2$, needles, m. p. 121° (monohydrochloride, m. p. 238° ; dihydrochloride, needles, m. p. 222°), which is reduced by sodium and boiling amyl alcohol to 4-amino-2:2-dimethyl-6-isobutylpiperidine, $C_{11}H_{24}N_2$, b. p. $147^\circ/65$ mm. (hydrochloride, $C_{11}H_{24}N_2 \cdot 2HCl$; acetate of the acetyl derivative, m. p. $143-144^\circ$). The base yields a carbamate by absorption of carbon dioxide, and is converted by nitrous acid into the preceding *cis*-alkamine, m. p. $91-92^\circ$.

By warming with acetic anhydride, 2:2:6-trimethyl-4-piperidone is converted into its *acetyl* derivative, prisms, m. p. 92° , which yields *acetylvinylthioacetonalamineoxime* (1-acetyl-4-oximino-2:2:6-trimethylpiperidine), m. p. 130° , by treatment with aqueous hydroxylamine.

[With A. ZART.]—Benzylidenethioacetonalamineoxime yields only products of fissive decomposition when reduced by zinc dust and alcoholic hydrochloric acid, but is converted by reduction with sodium and boiling amyl alcohol into β -4-amino-2-phenyl-6:6-dimethylpiperidine, six-sided plates softening at 60° , no definite m. p., b. p. $183^\circ/36$ mm., which is isolated as the *hydrobromide*, $C_{13}H_{20}N_2 \cdot 2HBr$, prisms with $3H_2O$, m. p. 75° , decomp. 100° ; the *hydrochloride*, *platinichloride*, *hydriodide*, and *picrate* are mentioned.

[With AUGUST BAUDREXEL.]— α -4-Amino-2:2:6-trimethylpiperidine and ethyl chloroformate react in cold ether to form the *hydrochloride*, $C_{11}H_{22}O_2N_2 \cdot HCl$, crystals, m. p. $244-245^\circ$, of

α-ethyl trimethylpiperidylcarbamate, b. p. 148—150°/12 mm. (*picrate*, m. p. 208—209°). Attempts to eliminate ethyl alcohol from the carbamate with the object of creating a bridge linking in the 1:4-position were unsuccessfully made with zinc chloride, fused sodium acetate, phosphoric anhydride, phosphoryl chloride, and concentrated hydrochloric acid. The *α*-aminotrimethylpiperidine reacts in ethereal solution with carbon dioxide to form the *carbamate*, $C_5H_7Me_3N \cdot NH \cdot CO_2H, NH_2 \cdot C_5H_7Me_3N$, m. p. 112°.

The following compounds of the *β*-series were prepared by similar methods: *β-ethyl 2:2:6-trimethylpiperidyl-4-carbamate*, b. p. 151—152°/12 mm., m. p. 68°, and its *hydrochloride*, m. p. 253—254° (decomp.), and *picrate*, m. p. 164—165°; *β-aminotrimethylpiperidine trimethylpiperidylcarbamate*, m. p. 92°.

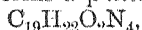
[With A. ZART.]—*α*- and *β*-4-Amino-2:2:6-trimethylpiperidine yield *dibenzoyl* derivatives, $C_{22}H_{26}O_2N_2$, m. p. 192—193° and 210—211° respectively, on benzoylation. The *α*-base reacts with phenylcarbimide in cold benzene to form the *phenyltrimethylpiperidylcarbamide*, $NHPh \cdot CO \cdot NH \cdot C_5H_7Me_3N$, needles, m. p. 211—212°, and with phenylthiocarbimide in ethereal solution to form the corresponding *thiocarbamide*, $C_{15}H_{23}N_3S$, crystals, m. p. 110°, whilst the hydrochloride of the *α*-base reacts with potassium cyanate in concentrated aqueous solution to form *α-trimethylpiperidylcarbamide*, $C_5H_7Me_3N \cdot NH \cdot CO \cdot NH_2$, leaflets, m. p. 55° (not sharp), decomp. below 100°. The corresponding substances in the *β*-series are *phenyltrimethylpiperidylcarbamide*, m. p. 130—138°, the *thiocarbamide*, $C_{15}H_{23}N_3S$, m. p. 160—161°, and *β-trimethylpiperidylcarbamide*, m. p. 170—171°.

[With HERBERT THOERL.]—Equal molecular quantities of 2:2:6-trimethyl-4-piperidone and ethyl chloroformate in ethereal solution, heated on the water-bath with a saturated solution of potassium carbonate, yield *ethyl 4-keto-2:2:6-trimethylpiperidine-1-carboxylate*, m. p. 34—35°, b. p. 141—142°/12 mm. (*oxime*, leaflets, m. p. 136°). The oxime is reduced by sodium amalgam and a mixture of alcohol, water, and acetic acid on the water-bath to *ethyl 4-amino-2:2:6-trimethylpiperidine-1-carboxylate*, b. p. 160°/12 mm., from which an internal 1:4-carbamide could not be produced.

The direct methylation of 2:2:6-trimethyl-4-piperidone at the imino-group is very difficultly effected. The result is attained indirectly, however, by oxidising *α*- and *β*-*N*-methylvinylidiacetonalkamines (see below) by chromic and acetic acids. Although the *α*-isomeride is very resistant to oxidation, both yield the same *N-methylvinylidiacetonamine* (1:2:2:6-tetramethyl-4-piperidone), b. p. 96—97°/14 mm., which is purified through the *hydrobromide*. It forms an *oxime*, prisms, m. p. 93° (*picrate*, needles, m. p. 216° [decomp.]).

[With AUGUST BAUDREXEL.]—The following derivatives have been prepared with the object of obtaining substances suitable for

the easy identification of the more important cyclic acetone bases, but none of them compares with the oxime for this purpose. 2:2:6-Trimethyl-4-piperidone forms a *semicarbazone*, $C_9H_{18}ON_4$, crystals, m. p. 196—197° (*osulate*, m. p. 182°), the triacetoneamine forms a *semicarbazone*, $C_{10}H_{20}ON_4$, crystals, m. p. 219—220°, whilst benzylidenediacetonamine forms a *p-nitrophenylhydrazone*,



m. p. 105—106°.

[With ARTHUR ZART.]—4-Hydroxy- α - and - β -1:2:2:6-tetramethylpiperidines are readily obtained by heating the 4-hydroxy-2:2:6-trimethylpiperidines with 40% formaldehyde on the water-bath. The hydrochloride of the α -compound reacts with benzoyl chloride at 120° to form α -4-benzoyl-1:2:2:6-tetramethylpiperidine, b. p. 194—195°/16 mm. (*hydrochloride*, m. p. 192°, *platnichloride*, m. p. 208° [decomp.], *nitrate*, and *picrate*, m. p. 180—181°). The corresponding β -benzoyl derivative has b. p. 195°/15 mm., and forms a *hydrochloride*, m. p. 58° (not sharp), *platnichloride*, m. p. 218° (decomp.), *nitrate*, m. p. 163° (decomp.), and *picrate*, m. p. 213°.

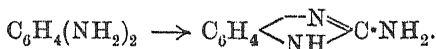
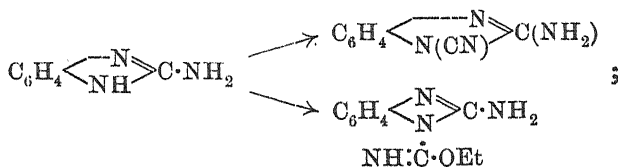
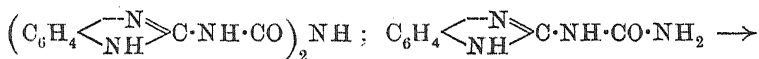
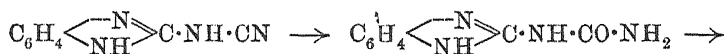
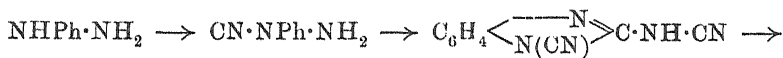
[With ERICH GROSCHUFF.]—The behaviour of cyclic acetone bases towards nitrous acid has been already published (A., 1901, i, 745).
C. S.

New Mode of Formation of Pyrrole-black. A. ANGELI and A. PIERONI (*Atti R. Accad. Lincei*, 1918, [v], 27, ii, 300—304. Compare A., 1918, i, 547).—Treatment of pyrrole with the calculated quantity of magnesium ethyl iodide in very dilute ethereal solution, and passage through the liquid of a gentle current of air for about twenty-four hours, yields a voluminous, very black powder, which may be obtained almost free from ash by treatment with dilute sulphuric acid. This substance is far more intensely black than the pyrrole-blacks obtained by methods previously described, and, like these and the natural melanins, it does not melt, but furnishes vapours which turn a pine splinter moistened with hydrochloric acid an intense red; it is insoluble in all ordinary solvents, and also in alkali solutions. It is slowly oxidised by hydrogen peroxide in acetic acid, or dilute aqueous permanganate, or dichromate and dilute sulphuric acid. The compositions of the different pyrrole-blacks obtained in various ways are given. The yellowish-white product formed, together with pyrrole-black, by the action of peracetic acid, is probably a derivative of tripyrrole, and its composition is in agreement with the formula $C_{12}H_{17}O_3N_3$. Like aniline-blacks, pyrrole-blacks react readily with phenylhydrazine.

T. H. P.

Action of Cyanogen Haloids on Phenylhydrazine. IV. Passage to Derivatives of *o*-Phenylenediamine. G. PELLIZZARI and AUGUSTO GAITER (*Gazzetta*, 1918, 48, ii, 151—182).—Further

investigations (compare A., 1892, 1323; 1907, i, 873 and 1911, i, 338) show that it is possible to effect the following series of changes :



αβ-Dicyano-o-phenyleneguanidine, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{N(CN)} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CN}$, obtained by the action of cyanogen bromide on *α*-cyanophenylhydrazine in presence of water and pieces of marble, forms white crystals, and turns yellow and then brown when heated, but does not melt at 300°; it reacts acid towards litmus, and emits ammonia when heated with alkali hydroxide. The sodium salt forms a crystalline magma, and the potassium salt a gelatinous mass.

β-Cyano-o-phenyleneguanidine, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CN}$, prepared by the action of potassium hydroxide on the preceding compound, forms long, thin, elastic, shining needles, and turns yellow at 240° and softens and decomposes at 250—260°; it has slightly acid properties and exhibits normal ebullioscopic behaviour in alcohol. It is highly resistant to the action of potassium hydroxide, and only in a sealed tube at 140° is it possible to detach the *β*-cyanogen group. Its *silver* salt was prepared and analysed.

o-Phenylene-β-guanilylcarbamide, $\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, obtained as hydrochloride by the action of hot dilute or cold concentrated hydrochloric acid, forms shining, colourless needles and becomes opaque, but does not melt at 300°. Its *hydrochloride*, $\text{C}_6\text{H}_4\text{ON}_4\cdot\text{HCl}$, decomposing at 255—260°, *platinichloride*, and *picrate* were prepared and analysed.

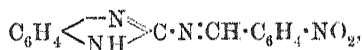
Diphenyleneguanylbiuret, $(\text{C}_6\text{H}_4\left\langle\begin{array}{c} \text{---N---} \\ \text{NH} \end{array}\right\rangle\text{C}\cdot\text{NH}\cdot\text{CO})_2\text{NH}$, obtained by heating the preceding compound at 180—200°, crystallises in slender needles.

o-Phenyleneguanidine, prepared by the action of hydrochloric acid on *o*-phenyleneguanilylcarbamide or *αβ*-dicyano-*o*-phenylene-

guanidine, is identical with the compound obtained from cyanogen bromide and *o*-phenylenediamine (compare Pierron, A., 1908, i, 926). The following salts were prepared and analysed: *carbonate*; *nitrate*, exploding without melting at 225°; *acetate*, m. p. 218°; *picrate*, m. p. 270° (decomp.); and *platinichloride*, + $\frac{1}{2}$ H₂O, which softens at 225°, and then melts and decomposes. The free base may be recognised by the alkaline reaction of its aqueous solution towards litmus and by the intense blue coloration, changing to green and then to brownish-yellow, obtained by the action of hypobromites or hypochlorites.

Acetyl-o-phenylenguanidine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix}\rangle\text{C}\cdot\text{NHAc}$, forms slender, white needles, m. p. 314—315° (decomp.). The action of nitrous acid on the corresponding benzoyl derivative (compare Pierron, *loc. cit.*) yields phenylencarbamide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix}\rangle\text{C}\cdot\text{OH}$ or $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}\rangle\text{CO}$.

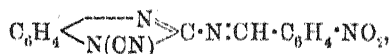
m-Nitrobenzylidenephnyleneguanidine,



prepared from *o*-phenyleneguanidine and *m*-nitrobenzaldehyde in presence of a drop of piperidine, forms minute, yellow needles, m. p. 170°.

α -Cyano-o-phenylenguanidine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N} \\ \text{N(CN)} \end{smallmatrix}\rangle\text{C}\cdot\text{NH}_2$, obtained from *o*-phenyleneguanidine and cyanogen bromide, forms long, colourless needles, and decomposes at 173—175°, rapidly in a moist atmosphere and slowly in a desiccator. Its *platinichloride* turns brown at 100° and undergoes change when boiled with water.

m-Nitrobenzylidene- α -cyano-o-phenylenguanidine,



prepared by the interaction of *α -cyano-o-phenyleneguanidine* and *m-nitrobenzaldehyde* in alcoholic solution in presence of a drop of piperidine, forms microscopic, yellow crystals and decomposes at 285—290°.

α -Ethoxy-o-phenylencarbiminoguanidine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}\rangle\text{C}\cdot\text{NH}_2$,
NH $\cdot\dot{\text{C}}\cdot\text{OEt}$

obtained together with the preceding compound, forms colourless needles, m. p. 155°. Its *platinichloride* forms pale yellow rhombs, m. p. 222—224° (decomp.). With *m-nitrobenzaldehyde* in presence of a drop of piperidine, the base yields *m-nitrobenzylidene- α -ethoxy-o-phenylencarbiminoguanidine*, C₁₇H₁₅O₃N₅, which crystallises in pale yellow needles, m. p. 205—206° (decomp.).

According to Pierron (*loc. cit.*), the action of cyanogen bromide (3 mols.) and sodium hydrogen carbonate (3 mols.) on *o*-phenylene-

diamine (1 mol.) yields a little phenyleneguanidine and a large proportion (120—140% of the phenylenediamine used) of iminodi-

carbonylphenyleneguanidine, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \begin{array}{c} \diagdown \quad \diagup \\ \text{C}=\text{N} \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{NH} \end{array} \text{CO} \cdot$ This

compound may be obtained also from phenyleneguanidine (1 mol.), cyanogen bromide (2 mols.), and sodium hydrogen carbonate (2 mols.), or from phenyleneguanidine and biuret. The mechanism of its formation is under investigation. T. H. P.

Simultaneous Biochemical Syntheses of Gentiobiose and of the two β -Glucosides of Glycol by Emulsin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 253—256).—From the products of the action of emulsin from almonds on a mixture of dextrose and ethylene glycol, in the molecular proportion of 2:1, in aqueous solution, the authors have isolated and characterised gentiobiose, glycyll β -glucoside, and glycyll β -di-glucoside. W. G.

Physiological Chemistry.

The Blood Sugar. GUSTAV KROK (*Biochem. Zeitsch.*, 1918, **92**, 84—89).—An analysis of the sugar in blood was made by Bang's micro-method, both before and after hydrolysis by acids in the case of rabbits, after ingestion of starch and of maltose (at varying intervals), and after administration of adrenaline, and a few similar analyses were made on the blood of the human subject. There was no appreciable difference in the reducing power before and after hydrolysis in any case, and the results give no support to Lépine's conception of the "sucre virtuel" of blood. S. B. S.

The Theory of Clotting. ALFRED PERUTZ and MAX ROSEMAN (*Biochem. Zeitsch.*, 1918, **92**, 90—95).—The amount of fibrin which is obtained by mixing serum and plasma stands in some proportional relationship to the amounts of these two components used, when they are employed in great dilutions. If diminishing amounts of serum are added to the same amount of plasma, the amount of fibrin formed diminishes. In the same way, diminishing amounts of plasma added to the same amount of serum also produce diminishing amounts of fibrin. If very great dilutions are employed of plasma and serum, so as to be near the limits of a reaction, in order that the reaction should take place at all, the serum concentration must be greater than the plasma concentration. S. B. S.

The Presence of Phosphates in Human Blood-serum. VII. JON. FEIGL (*Biochem. Zeitsch.*, 1918, **92**, 1—83).—The author gives a very extensive and detailed review of the methods of separating the constituents which contain phosphorus in the blood, especially the lipid phosphorus and inorganic (acid soluble) phosphorus, giving in particular a detailed criticism of the recent methods of Bloor, Greenwald, and their collaborators. He also gives a critical account of the micro-methods for estimating the phosphorus after ashing, including the various nephelometric and colorimetric methods. He gives, finally, a series of tables of analyses of the phosphorus of the blood (chiefly lecithin phosphorus) in pathological cases obtained by himself by the employment of various methods. S. B. S.

Shark and Ray Liver Oils. M. TSUJIMOTO (*J. Chem. Ind., Tokyo*, 1918, **21**, 1015—1042).—The analytical values of the liver oils of thirteen species of Japanese sharks and five species of Japanese rays are given. The oil derived from the shark *Pristiurus pilosus* had an exceptionally high iodine value (309.0) and a very low sp. gr. (D_4^{15} 0.8664). It was found that all the shark liver oils of low sp. gr. (below 0.9) contained the hydrocarbon squalene, which was also present in the egg oils of two species of shark, but it was not a constituent of any of the ray liver oils. [See also *J. Soc. Chem. Ind.*, 1919, 109A.] C. A. M.

Genesis of Thiocyanic Acid in Animals. V. SERAFINO DEZANI (*Arch. Farm. sper. sci. aff.*, 1918, **25**, 278—288; from *Chem. Zentr.*, 1918, ii, 836—837).—The quantity of thiocyanic acid formed in the dog depends on the albumin content of the food; this result is in striking contrast with the experience of Bruylants and Grober with the human subject.

After administration of acetonitrile, thiocyanic acid could be detected in the blood serum and saliva of the dog as soon as in the urine; its formation cannot therefore in any case be an exclusive function of the kidneys. H. W.

Calcium—Form of Reserve in the Female of the Phasmides; its Forms of Elimination in the two Sexes. J. PANTEL (*Compt. rend.*, 1919, **168**, 242—244).—Calcium exists as a reserve in the form of its carbonate in the lower malpighian tubes of the females of the Phasmides. In both sexes, the principal form in which it is eliminated is as its phosphate, accessory forms being the oxalate and probably the urate. W. G.

Catalytic Action of Serpent Venoms on the Nucleic Acids. C. DELEZENNE and H. MOREL (*Compt. rend.*, 1919, **168**, 244—246).—Both plant and animal nucleic acids are hydrolysed by venoms from members of the Colubridae and Viperidae groups. The curves showing the velocity of the reaction indicate that the reaction is catalytic, and it has been shown that the amount of

hydrolysis is independent of the amount of venom used. The optimum temperature is 50--52°, and the venom loses its hydrolytic powers if heated for a few minutes at 100° or if to the medium is added specific antivenom serum. The different venoms vary in the intensity of their catalytic action, this variation being in the same direction as is that of their toxicity. W. G.

The Guttameter and its Application to the Study of Drugs and Poisons. FRIEDRICH ESCHBAUM (*Ber. Deut. pharm. Ges.*, 1918, 28, 397—416).—The guttometer is a capillary pipette with a wide delivery orifice from which ten drops are collected in a weighing bottle and the weight recorded. The instrument is standardised with water at 20°, ten drops of which should weigh 1.20 grams. The weight of ten drops of the liquid, corrected by the factor of standardisation of the instrument, is proportional to the surface tension; thus the results are inversely proportional to those obtained with the stalagmometer. The author has extended certain observations of Traube and others on the use of this instrument, from which it was deduced that the toxicity of solutions of alkaloids is in direct relation to the lowering of the surface tension of water produced by the alkaloid at standard concentration. Thus a number of derivatives of the quinine alkaloids have been studied and ranged in the order of decrease in surface tension produced in 0.1% solutions of their salts mixed with increasing small proportions of sodium carbonate. The order of classification so obtained coincides with that of increasing toxicity. Quinine and quinidine, approximately equal, had the least effect on surface tension; stronger depressions were recorded in the following order: hydroquinine, ethylhydrocupreine, ethylapohydroquinidine, isoamylhydrocupreine, and iso-octylhydrocupreine. The depression of the surface tension increases with the amount of alkali added. Morphine and apomorphine occupy a peculiar position among the alkaloids in that solutions of their salts, when treated with sodium carbonate, do not show a depression of the surface tension as compared with water. It is shown, however, that morphine salts when treated with certain small proportions of ammonia liberate the alkaloid in a disperse form, and a depression of the surface tension is then observed. J. F. B.

Chemistry of Vegetable Physiology and Agriculture.

Action of Stimulants on Nitrifying Bacteria. C. MONTANARI (*Staz. sper. agr. ital.*, 1917, 50, 69—72; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1914, i, 1159).—The action of compounds of copper, barium, lead, zinc, and arsenic has been investigated in extension of the work on manganese salts. The addition produces

different effects according as it takes place at the commencement of the experiment or when development of the nitrate ferment has occurred. In the former case, the formation of nitrates is hindered by small amounts of copper or by larger quantities of the other substances, whilst in the latter case the ferment is damaged by large doses of arsenic or, to some extent, of copper. Nitrification was not rendered more vigorous by minimal doses of the different substances, except in the solitary instance of manganese sulphate.

H. W.

The Chemistry of the Higher Fungi. XIII. *Scleroderma vulgare*, Fr., and *Polysaccum crassipes*, D.C. JULIUS ZELLNER (*Monatsh.*, 1918, **39**, 603-615. Compare A., 1915, i, 1086; 1918, i, 54).—Extraction of *Scleroderma vulgare*, Fr., with light petroleum yielded a deep brown, viscous mass containing an ergosterol and a resin. The ethereal extract contained fumaric acid, and further quantities of an ergosterol, which was not isolated in the pure state. Mannitol, dextrose, choline, and an amorphous carbohydrate were isolated from the alcoholic extract. Viscosin and potassium phosphate were isolated from the aqueous extract, in which neither invertases nor diastases could be detected.

Polysaccum crassipes, D.C., was similarly successively extracted with (1) light petroleum, (2) ether, (3) alcohol, and (4) water. The first extract was a dark brown, viscous mass rich in unsaponifiable matter, consisting of ergosterols and a reddish-brown resin. The second extract consisted of ergosterols; the presence of fumaric acid could not be definitely established. The third extract yielded dextrose, choline, and the potassium ammonium salt of a tannin-like acid (the free acid and its silver and copper salts are described), which probably has a glucosidic structure. The fourth extract contained a carbohydrate similar to that obtained from *Scleroderma*, together with mineral matter; the presence of ferments (invertase, maltase, diastase) could not be established.

H. W.

The Researches of Willstätter on the Assimilation of Carbon Dioxide. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 1138-1146).—A critical summary of the more recent work of Willstätter on the mechanism of the absorption and decomposition of carbon dioxide by chlorophyll.

W. S. M.

Action of Vegetable Enzymes on certain Organic Compounds. G. CIAMIGIAN and C. RAVENNA (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 293-300).—Much of this paper has been already published, the results not included in the previous abstract (this vol., i, 58) being briefly as follows.

Benzoic acid is not changed by the enzymes of pulped spinach leaves, but salicylic acid is largely oxidised; the respective sodium salts behave similarly. Coumarin remains unaltered, but mandelic acid is converted by spinach in an atmosphere of oxygen into a

compound which is not extracted by ether, but is reconverted into the original acid by boiling dilute sulphuric acid; in carbon dioxide, mandelic acid remains unaffected. Just as by the action of light, oxalic acid is almost completely oxidised by the enzymes, whilst succinic acid, which in the light is oxidised to a slight extent to glyoxal, acetaldehyde, acetic, and perhaps propionic acid, with the spinach enzymes yields acetaldehyde and a compound giving succinic acid when treated with emulsin. Lactic acid, which forms acetaldehyde and acetic acid on auto-oxidation in the light, yields only acetaldehyde under the action of the spinach. Malic acid, which gives formaldehyde, acetaldehyde, formic and acetic acids, and certain undefined products under the influence of light, yields only acetaldehyde with these enzymes.

Acetone is oxidised, as by light, to acetic and formic acids and formaldehyde, whilst methyl ethyl ketone gives propionic and formic acids under the influence of the spinach, its behaviour in light being unknown. The action of light on cyclic ketones results in hydrolysis to the corresponding aliphatic acids, and also in the formation of the corresponding dibasic or ketonic acids, whereas the action of the spinach enzymes converts these ketones into lower aliphatic acids and sometimes into succinic acid, the acids corresponding with the ketones used being never obtained. Thus, *cyclohexanone* gives formic acid and a mixture of volatile acids, apparently propionic and butyric. 2-Methyl*cyclohexanone* and 3-methyl*cyclohexanone* yield propionic and formic acids, and 4-methyl*cyclohexanone*, acetic acid, in addition. Menthone gives succinic, formic, acetic, and probably propionic acids. Pyridine, piperidine, nicotine, strychnine, and caffeine are not affected by the spinach enzymes, but morphine, quinine, and cinchonine undergo oxidation to a considerable extent.

Some of the compounds, such as benzoic acid, pyridine, piperidine, and nicotine, which resist attack by the enzymes of spinach, disappear when they are injected into maize and tobacco plants (*loc. cit.*). In one experiment, in which a total of 36 grams of sodium benzoate, corresponding with 30.5 grams of benzoic acid, were inoculated into twenty-five maize plants, 21.6 grams of the acid were afterwards found to have disappeared, and the plants yielded a distillate containing formic, acetic, and propionic acids in amounts corresponding approximately with the benzoic acid attacked.

T. H. P.

Biochemical Changes due to Environment. OTTO ROSENHEIM (*Biochem. J.*, 1918, 12, 283—289).—The inflorescence of edelweiss (*Leontopodium alpinum*) contains a chromogenic substance, probably a flavone, which is not in glucosidic combination. It is best extracted with 90% alcohol at 70—75°. A comparative estimation of the amount present in plants grown in London at an altitude of 80 m. and in plants collected in the Alps at an altitude of 2000 m. shows the ratio of amounts present to be roughly as

1:4, and in addition the plants grown in the Alps contained traces of the chromogenic substance in glucosidic combination. These results show the biochemical adaptation of Alpine plants to changed environment, and support Shibata's hypothesis that the biological significance of flavones in the plant consists in their protective action against the injurious influence of ultra-violet light.

W. G.

Essential Oil and Wax of Shuei Flower (*Jasminum odoratissimum*). R. TSUCHIHASHI and S. TASAKI (*J. Chem. Ind., Tokyo*, 1918, **21**, 1117—1143).—Fresh flowers of Shuei (*Jasminum odoratissimum*), cultivated in Formosa and used for perfuming tea, yielded on extraction with light petroleum 0.277% of concrete essence, which on maceration with alcohol was separated into 0.116% of essential oil and 0.166% of flower wax. The oil contained approximately 6% of *d*-linalool, 6% *d*-linalool acetate, 6% benzyl alcohol, 1.6% benzyl acetate, methyl ester of anthranilic acid and indole (10%), and constituents of high boiling point (possibly sesquiterpene alcohol or diterpene alcohol) about 57%. [See also *J. Soc. Chem. Ind.*, 1919, 117A.]

C. A. M.

The Absorbent Power of Dry or Moist Earth with respect to Chlorine Gas. DANIEL BERTHELOT and RENÉ TRANNOY (*Compt. rend.*, 1919, **168**, 121—123).—Dry sand absorbs chlorine badly, but a peaty soil or leaf mould has very marked absorbent properties for this gas. The absorptive power is markedly increased by moistening the soil with 10% of its weight of water. Any further addition of water only causes an increased absorption, due to the water added.

W. G.

Connection between Absorption and Coagulation and its Relation to the Inorganic Colloids of the Soil. III. A. DE DOMINICIS and P. CHIARIERI (*Staz. sper. agr. ital.*, 1917, **50**, 451—479; from *Chem. Zentr.*, 1918, ii, 854. Compare A., 1915, i, 859; 1916, i, 240).—The previous results, that the action of electrolytes on the unstable hydrosols causes a single process resulting in coagulation through absorption, are confirmed by a series of experiments with the metals of the alkaline earths. When particles and ions with opposite charges come into contact, mutual attraction occurs, resulting in neutralisation of the charges and formation of absorption compounds. Decrease in concentration consequently follows both in colloidal and ionic-molecular solution. The physico-chemical properties of the soil are invariably favourably influenced with regard to fruitfulness by this phenomenon.

H. W.

The Organic Phosphorus of Soil. R. S. POTTER and R. S. SNYDER (*Soil Sci.*, 1918, **6**, 321—332. Compare Potter and Benton, A., 1917, i, 76).—For the most part a reply to Gortner and Shaw (compare A., 1917, i, 376). The authors have prepared the curves for the hydrolysis of phytin and of nucleic acid by 5%

sulphuric acid at 100°, and show that both these reactions are of the first order. No definite conclusions could be drawn from the curves for the hydrolysis of the organic phosphorus of three soils, but the direction of the curves was such as to indicate that the organic phosphorus might have been due to phytin or to a pyrimidine nucleotide.

W. G.

The Presence of Aluminium as a Reason for the Difference in the Effect of so-called Acid Soil on Barley and Rye.

BURT L. HARTWELL and F. R. PEMBER (*Soil Sci.*, 1918, 6, 259—279).—The authors find that although rye will grow far more satisfactorily on an acid soil than will barley, seedlings of both these crops are equally affected by a given amount of acidity, both in water and sand cultures. The authors attribute the different effect of the acid soil on the two crops to the presence of aluminium sulphate in the soil solution, and they show that equivalent amounts of aluminium sulphate and sulphuric acid when added to an optimum nutrient solution produce about the same depression on barley seedlings, and that whilst a similar depression of the rye crop is produced by the acid, the aluminium sulphate causes very little depression and scarcely affects the rye roots. Further, as the hydrogen-ion concentration of the nutrient solution containing the aluminium sulphate was only about one-fourth of that containing the acid, they conclude that aluminium exerts a toxic effect on the barley. This active aluminium may be largely removed from the soil solution by the application of lime or phosphates, even acid phosphates.

W. G.

Experiments with various Nitrogenous Fertilisers.

EILH. ALFRED MITSCHERLICH, S. VON SAUCKEN, and F. IFFLAND (*J. Landw.*, 1918, 66, 187—198).—Sand cultures of oats were treated with one and the same fertiliser, composed of magnesium and potassium sulphates, sodium chloride, and calcium phosphate, the nitrogen in the different cultures of a series being supplied in the form of sodium nitrate, ammonium sulphate, "Kalkstickstoff," carbamide, and carbamide nitrate. The results show that carbamide and its nitrate are at least equivalent in manurial value to the old nitrogenous fertilisers. Owing to its ready solubility in water, carbamide nitrate should serve, without causing marked plasmolytic phenomena, and hence injuries to the plants, as an excellent top-dressing, and may certainly replace sodium nitrate for this purpose. The yields of straw and corn under the different treatments are given in the form of tables, and are also subjected to analysis.

T. H. P.

Influence of Two Different Nutriment on the Yield of Crops. EILH. ALFRED MITSCHERLICH (*Landw. Jahrb.*, 1918, 52, 279—296; from *Chem. Zentr.*, 1918, ii, 854—856).—I. *Influence of two nutriment which are without mutual action.*—The effect of variation in the amounts of potassium and nitrogen on the growth

of oats has been investigated, use being made of potassium sulphate and ammonium nitrate. The factor of activity of the nitrogen is constant ($=1.14$) and independent of the amount of potassium; similarly, the factor of the potassium ($=2.48$) is constant and independent of the quantity of nitrogen. If the nutriment is present in an equally assimilable form (which may be assumed to be the case with salts which are soluble in water), and if they are not influenced by any external factor, it follows that, in order to secure an equal yield of oats, 2.18 times ($2.48/1.14$) as much nitrogen as potash must be supplied; potassium is better utilised than nitrogen by the plant.

II. *Influence of two nutriments which react with one another.*

---Alterations in the increase in yield obtained by addition of either nutriment are immediately observed when the nutriment is either chemically or physically affected by other substances which are possibly introduced in the manuring, but which can be present in every possible combination in the soil in agricultural practice.

(a) *Chalk and phosphoric acid.*—Experiment shows that an equally good yield cannot be obtained by manuring with raw phosphate as with a readily soluble manure. Further, the maximum yield which can be obtained with a phosphate manure is diminished slightly at first, but more rapidly subsequently, by addition of chalk, and, finally, as is shown by experiments with phosphorite meal, to such an extent that an increase in yield due to the phosphate manure is scarcely noticeable. The value of different phosphate manures is affected in an extraordinary manner by the addition of chalk. Thus, the activity of tricalcium phosphate is diminished to considerably greater extent than that of a Thomas meal phosphate by addition of chalk; the value of the latter, however, does not remain constant, since a good specimen is found to be less affected than one of poorer quality. The relative value of tricalcium phosphate and Thomas meal T. in the absence of chalk is approximately the same as that previously found when calcium was added in large quantity in the form of calcium nitrate. Phosphatic manure loses much of its value if applied to land recently treated with chalk or marl or to soil rich in chalk unless other salts, such as ammonium sulphate, are also used. Manures which contain phosphates in a slightly soluble form are less effective in the presence of potash than those containing more soluble forms; raw phosphate is probably useless on land rich in chalk. It is doubtful if a preliminary manuring with phosphoric acid has any practical result. (b) *Potash and ammonium chloride.*—It has been previously found that the application of ammonium chloride, when sufficient nitrogen for nutriment is otherwise present, diminishes the value of manuring with potash; this result is now confirmed, and it appears to be not impossible that, under the given conditions, the ammonium chloride is physiologically acid, and therefore poisonous.

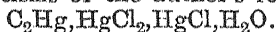
H. W.

Organic Chemistry.

The Influence of Catalysts on the Chlorination of Hydrocarbons. V. R. KOKATNUR (*J. Amer. Chem. Soc.*, 1919, 41, 120—124).—Attempts were made to prepare pentachloroethane by the limited chlorination of *s*-tetrachloroethane. Various catalysts, such as vegetable and animal charcoal and metallic iron, were suspended in *s*-tetrachloroethane, and chlorine gas was passed through the liquid at various temperatures. In no case was pentachloroethane found among the products of the reaction, which consisted only of hexachloroethane and unchanged tetrachloroethane. In other trials, chlorination was effected by heating with bleaching powder and water and with anhydrous aluminium chloride. In these cases, also, hexachloroethane only was produced, although a certain amount of the tetrachloroethane was converted into *as*-tetrachloroethane. It is not decided whether this complete chlorination, giving hexachloroethane as the only product, is to be ascribed to the influence of catalysts or to the symmetrical structure of the tetrachloroethane, whereby both atoms of hydrogen are equivalent in function and are therefore substituted simultaneously. It is true that pentachloroethane may be produced by chlorinating in the presence of actinic light, but that may be due to the specific influence of the light on the constitution either of the *s*-tetrachloroethane, making it unsymmetrical, or of the chlorine molecule.

J. F. B.

Constitution of the Product of the Action of Acetylene on Mercuric Chloride. W. MANCHOT (*Annalen*, 1918, 417, 93—106. Compare Manchot and Haas, A., 1913, i, 1009).—A reply to Biltz and Reinkober's criticisms of the author's formula,



[With FRANZ MÄHRLEIN.]—Styryl ethyl ether and an aqueous solution of mercuric acetate (3 mols.) are warmed at 50°, the cooled liquid is poured, after two hours, into a 10% solution of sodium chloride, whereby a white substance, $\text{CHPh}:\text{CH}:\text{OH}, 2\text{HgCl}:\text{OH}$, is obtained. It melts partly at about 120°, decomposes somewhat violently when heated over a free flame, is scarcely attacked by dilute sodium hydroxide solution, and yields phenylacetaldehyde by heating with hydrochloric acid.

In view of the preceding observations, the author now inclines to the opinion that the product of the action of acetylene on mercuric chloride, Biltz and Mumm's "trichloromercuriacetaldehyde," is an additive product of vinyl alcohol; a formula is not recorded, on account of the uncertainty of the individual character of the substance.

C. S.

Constitution of Geraniol, Linalool, and Nerol. ALBERT VERLEY (*Bull. Soc. chim.*, 1919, [iv], 25, 68—80).— α -Citral when boiled with 1% aqueous sodium hydroxide gives β -methyl- Δ^8 -heptenone, $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}$, b. p. 168° , which when oxidised with potassium permanganate gives the glycol, $\text{HO}\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}$, which when oxidised with chromic acid only gives traces of acetone. β -Methyl- Δ^8 -heptenone when warmed on a water-bath with dilute sulphuric acid is readily transformed into its Δ^6 -isomeride, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}$ (compare Tiemann, *Ber.*, 1895, 28, 21, 2126). From these facts, the author assigns to geraniol, obtained by the reduction of citral, the constitution $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, which corresponds with citronellol. With hydrogen bromide, this geraniol gives a tribromo-compound,

$\text{CH}_3\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$,
which by treatment with alkali yields isolinalool, b. p. 200 — 207° , which thus has the constitution

$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$,
ordinarily assigned to linalool, which must, therefore, be represented by the formula $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_2$. With hydrogen iodide, geraniol gives a moniodo-derivative, which under the influence of alcoholic sodium hydroxide readily loses hydrogen iodide, giving a quantitative yield of nerol, to which the author assigns the constitution

$\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$,
previously attributed by Tiemann to geraniol. Nerol when oxidised with dilute chromic acid mixture gives *neral*, b. p. $120^\circ/20$ mm., D 0.890, which is easily decomposed by alkalis, giving acetaldehyde and β -methylheptenone, and with an alkaline solution of cyanoacetic acid yields *nerylidenecyanoacetic acid*, m. p. 95° .

Of the substances of the geranic series occurring in nature, geraniol, citral, linalool, and methylheptenone, there exist two isomeric forms, α and β , of which the α -form is much the more abundant of the two, being accompanied by only a very small proportion of the β -form.

The new formula for geraniol given above permits of a ready explanation of the close relationship which exists between geraniol and dipentene, $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH} \end{matrix}\text{CMe}$. W. G.

Molecular Transpositions of α -Glycols. I. Introduction. A. ORSKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 9—19).—A theoretical discussion in which the author shows that Werner's theory (A., 1906, i, 436) combined with that of Tiffeneau (A., 1906, i, 724) can be successfully applied to the interpretation of the phenomena of the transpositions occurring in the dehydration of α -glycols. He attributes to each radicle an "aptitude for migration," or a "relative mobility" and a "saturation capacity" which vary with the different radicles, but in the same sense, and assumes that these control the transpositions, according to which he shows

that the symmetrical and asymmetrical isomeric glycols give the same products of dehydration:



These transpositions may, however, be modified by the nature of the dehydrating agent, and in the case where R or R' is a phenyl group by the introduction of substituents into the benzene nucleus. The benzyl group apparently has a smaller "mobility" and a smaller "capacity of saturation" than the phenyl group. W. G.

Preparation of Methyl Sulphate. WALTER NORMAN HAWORTH and JAMES COLQUHOUN IRVINE (Brit. Pat., 122498).—For the production of methyl sulphate, dimethyl ether and sulphur trioxide are caused to combine directly in the presence of a solvent. The sulphur trioxide may, if desired, be employed in the form of the dilute gas produced by the reaction of sulphur dioxide with air by the contact process. Both the sulphur trioxide and the methyl ether vapours must be perfectly dry, and the latter must be free from the vapours of alcohol. The two gases are passed simultaneously in approximately equimolecular proportions into the solvent liquid, which may conveniently consist of methyl sulphate itself. The mixture is stirred continuously and cooled by a water-jacket or coil. The methyl sulphate produced is drawn off and treated with iron filings or other reducing agent to neutralise the influence of any excess of sulphur trioxide which may be present; it is then purified by rectification under diminished pressure.

J. F. B.

Preparation of Acetic Acid from Acetylene. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 297442; from *Chem. Zentr.*, 1919, ii, 61).—Acetylene is treated with solutions of hydrogen peroxide, persulphuric acid or monopersulphuric acid, or solutions or suspensions of their salts in acids in the presence of mercury or mercury compounds. Thus a quantitative yield of acetic acid is obtained in a single operation when acetylene is treated with solutions or suspensions of persulphates in water or acids in the presence of mercury or mercury compounds. Salts of monopersulphuric acid, solutions of persulphuric acid and monopersulphuric acid, and of hydrogen peroxide may also be used; in place of the latter, any substance (percarbonates, peroxides) may be employed which yields hydrogen peroxide when acidified.

H. W.

Manufacture of Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 112765).—The reaction between acetylene and glacial acetic acid for the production of ethylidene diacetate is caused to take place in the presence of aromatic or aliphatic sulphonic acids and mercuric acetate, and in the absence of mineral acids or acid salts of mineral acids. The formation of tarry by-products and the secondary decomposition of the ethylidene diacetate are thereby suppressed. Suitable acids are benzene-

sulphonic, naphthalenesulphonic, camphorsulphonic, sulphoacetic, methionic acids, etc. Forty parts of mercuric oxide are dissolved in 200 of glacial acetic acid, a solution of 50 parts of β -naphthalenesulphonic acid in 200 of glacial acetic acid is added at 70°, and the mixture is caused to absorb 200 parts of acetylene during two hours at 70°. The excess of acetic acid is then separated from the ethylidene diacetate in the usual way. J. F. B.

Preparation of the Bromoisovaleric Ester of Bromoamylene Hydrate. EMIL RATH (D.R.-P. 309455; from *Chem. Zentr.*, 1919, ii, 61).—The ester is obtained as a pale yellow oil of faint, characteristic odour, which can be distilled in a vacuum by heating a molecular mixture of bromoamylene hydrate and bromoisovaleryl bromide in the presence of an indifferent solvent at the temperature of the water-bath until hydrogen bromide ceases to be evolved; bromoisovaleryl chloride may be used in place of the corresponding bromide. H. W.

Theory of Acids. O. HINSBERG (*J. pr. Chem.*, 1918, [ii], 98, 145—154).—Elaborating the conception of multiple valency centres (A., 1917, ii, 173, 461; 1918, ii, 106), the author endeavours to correlate the acid properties of ethyl acetoacetate, oxy-acids, acetylene, hydrogen cyanide, hydrogen sulphide, and the halogen acids. Acids are compounds which contain hydrogen bound either alone (HCl; H₂S) or with other elements (oxy-acids; ethyl acetoacetate; hydrogen cyanide) to an element of groups V—VII of the periodic table. The acidic hydrogen atom is linked to one atom by a principal valency and to other atoms by several subsidiary valencies, the effect of this competition of forces being to render the hydrogen atom mobile.

The mobility and loose binding of the hydrogen atom within the acid molecule may be regarded as the preliminary condition for dissociation into anion and cation. C. S.

Nitration of Sucrose : Sucrose Octanitrate. E. J. HOFFMAN and V. P. HAWSE (*J. Amer. Chem. Soc.*, 1919, 41, 235—247).—After removal of acid, the product of the nitration of sucrose by sulphuric and nitric acids in the cold forms a tough, viscous, semi-transparent, slightly hygroscopic mass, which can be pulverised to a sticky, white powder when hardened by cooling. When heated and allowed to cool, it begins to flow sluggishly at 40° and then gradually sets, until at 8° it becomes very hard and brittle. When acid-free, it is fairly stable, and may be kept without appreciable change for weeks at the ordinary temperature, but it decomposes when heated at comparatively low temperatures, this decomposition becoming more rapid after long heating; it is very sensitive to friction or impact. The mean nitrogen content of different preparations was 15%, the molecular weight in freezing acetic acid, benzene, or nitrobenzene, 428.9—565.2, and the specific rotation, using light from a frosted tungsten lamp filtered through 6% dichromate solution, $[\alpha]^{20} + 56.66^\circ$.

Sucrose octanitrate, $C_{12}H_{14}O_3(NO_3)_8$, obtained by evaporation of the alcoholic solution of the above product at the ordinary temperature, forms elongated, acicular crystals, probably of the monoclinic, but possibly of the orthorhombic, system [HERBERT INSLEY], m. p. 85.5° , $[\alpha]^{20} + 56.05^\circ$; it has the normal molecular weight in freezing nitrobenzene, and when heated gradually from 33° to 87° in a period of nearly two hours it shows no signs of decomposition. Photomicrographs of the crystals are given. Sucrose octanitrate may be estimated in explosive mixtures by means of its rotatory power and nitrogen content (15.95%). T. H. P.

Preparation of Soluble Starch. JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 113—120).—Starch may be entirely converted into soluble starch, without the formation of erythro-dextrin or other cupric reducing products, by boiling with alcoholic hydrochloric acid under carefully regulated conditions. These conditions have been studied, and the method adopted by the author consists in suspending 20 grams of starch in 100 c.c. of 95% alcohol, adding 0.75 c.c. of strong hydrochloric acid (D 1.19), and boiling for exactly ten minutes with continuous agitation. The conversion is stopped by adding all at once the previously determined quantity of sodium hydrogen carbonate solution necessary to neutralise the acid. The soluble starch is then washed several times with alcohol by decantation, collected on a filter, and dried. The experiments performed in establishing the conditions of the above method of preparation showed that the amount of hydrolysis bears a direct ratio to the concentration of the hydrogen ion, but it would appear that in favourable circumstances the complete conversion into soluble starch constitutes a definite stage preliminary to further hydrolysis, and that maltose is not split off from the starch molecule as a direct consequence of this change. This supports the idea that soluble starch is a hydrated starch. From soluble starch onwards, the hydrolysis again appears to bear a direct ratio to the acid concentration. J. F. B.

Relations between the Viscosity of Cellulose Nitrate Solutions and the Nitration Process, with Special Reference to Wood Cellulose. G. LEYSIEFFER (*Koll. Chem. Beihefte*, 1918, **10**, 145—178).—The material employed was a chemically pure wood cellulose prepared from deal. It contained α -cellulose 80.4, β -cellulose 6.8, γ -cellulose 12.8%. The ash amounted to 0.20% and the fat to 0.44%. The nitration with a mixed acid of known composition was performed much in the usual manner; both cold and hot washing were employed. The drying was effected at 36 — 40° for twenty-two hours. The nitrogen content of the product was estimated by the Schulze-Tiemann method, and the nitrates were further characterised by solubility determinations in alcohol or ether-alcohol (2:1). The viscosity of the acetone solutions of the nitrates was determined by the Ost viscosimeter.

As the results of a large number of experiments, tables and

graphs of which are given, the following conclusions are drawn: (1) By the nitration of cellulose, the same value for the viscosity is always obtained provided all the factors which influence the internal friction (composition of the nitrating acid, temperature of the bath, duration of the nitration, proportion by weight of cellulose to acid, method of preparation and properties of the cellulose employed) are kept constant. (2) The greater the nitric acid content of a nitrating acid, the higher is the viscosity of the nitrated cellulose in acetone solution. If, however, the percentage content of nitric acid equals or exceeds that of the sulphuric acid, smaller values are found for the internal friction. This diminution is more marked in the case of dilute nitrating acids than of concentrated nitrating acids. Increasing the water content from 0% to about 11% causes an increase of the viscosity, only, however, if the nitric acid content is less than the sulphuric acid content; otherwise, and if the water content exceeds the above limit, smaller values are obtained for the viscosity. (3) Nitration at temperatures below 0° produces nitrates having high viscosity values. The higher the temperature of nitration, the smaller is the viscosity. (4) The viscosity values vary considerably in the case of nitrates which have been nitrated for only a short time (five to thirty minutes). They increase so long as the nitrogen content increases, but prolonged action of the nitrating acid results in a diminution of the viscosity. (5) A close connexion is found between the nitrogen content of a cellulose nitrate and the internal friction of its acetone solution: the higher the nitrogen content, the higher is the viscosity. (6) Acetone solutions of cellulose nitrates become more inobile with keeping, strongly viscous solutions more so than less viscous solutions. (7) The kind, method of preparation, and previous treatment of a cellulose are of great influence on the viscosity. A high content of γ -cellulose causes increased viscosity in the nitrate. Nitrates from cotton cellulose show higher viscosities than those from wood cellulose. C. S.

The *n*-Butylarylamines. III. Constitution of the Nitro-derivatives of *n*-Butyl-*p*-toluidine. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1919, 115, 175—181).

Amino-acids. HENRY DRYSDALE DAKIN (*Biochem. J.*, 1918, 12, 290—317).—By using a new method of extraction, the author has isolated a new aminohydroxy-acid and a new peptide from the products of acid hydrolysis of caseinogen.

When caseinogen is hydrolysed with sulphuric acid, and the latter subsequently removed as barium sulphate, on submitting the neutral concentrated solution of amino-acids to continuous extraction with butyl alcohol, it is found that five fractions can be obtained, as follows: (1) Monoamino-acids, both aliphatic and aromatic, which, although insoluble in butyl alcohol, are extracted in the above process, but deposited as a cream-coloured, granular powder in the extraction flask. (2) Proline, soluble in alcohol and extracted by

butyl alcohol. (3) Peptide anhydrides (diketopiperazines), extracted by butyl alcohol, but separated from (2) by their sparing solubility in alcohol or water. (4) Dicarboxylic acids, not extracted by butyl alcohol. (5) Diamino-acids, not extracted by butyl alcohol, but separable from (4) by phosphotungstic acid and other means. It is noteworthy that no indications of racemisation of the products during this process have been observed, and materially higher yields of many amino-acids were obtained than by existing methods. The fact that the monoamino-acids, which are essentially insoluble in all alcohols, are extracted by butyl alcohol under the above conditions, is due to the passage of a certain amount of water into the alcohol, since the extraction is very unsatisfactory if the aqueous solution of amino-acids contains an excess of salts, such as calcium chloride.

Using this method, the author found as an average of five determinations 8.0% proline from caseinogen, and from his specimen he prepared 1-prolylthydantoin, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH} \cdot \text{CO} \\ \text{CH}_2 \cdot \text{N} - \text{CO} \end{smallmatrix} > \text{NH}$, m. p. 165—167°, $[\alpha]_D^{20} - 232^\circ$ to -238.5° , by passage through the uramido-acid.

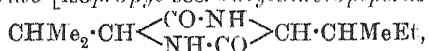
The method of extraction with butyl alcohol furnishes a ready means of obtaining a dry, almost neutral amino-acid mixture, which would serve as a basis for nutrient media with or without the addition of tryptophan, and might possibly find use for dietetic purposes, since most of the amino-acids which furnish dextrose in the diabetic organism are absent.

After the precipitation of the diamino-acids from the amino-acids not extracted by butyl alcohol, and subsequent separation of glutamic and aspartic acids, the former as its hydrochloride and the latter by the method of Levene and Van Slyke (compare A., 1910, i, 719), using freshly precipitated lead hydroxide, it was found that large amounts of at least one other dicarboxylic acid were still present, and it could be isolated. This acid, isolated through its silver salt, was characterised as β -hydroxyglutamic acid, $\text{CO}_2\text{H} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, crystallising in stout prisms. It is optically active and extremely soluble in water. It yielded silver, copper, mercury, lead, cadmium, zinc, calcium, and barium salts, gave a diethyl ester, and on prolonged heating at 100—110° over phosphorus pentoxide lost a molecule of water,

giving a compound, $\text{CO} < \begin{smallmatrix} \text{NH} \cdot \text{CH} \cdot \text{CO}_2\text{H} \\ \text{CH}_2 \cdot \text{CH} \cdot \text{OH} \end{smallmatrix} >$. On heating the acid with zinc dust, an intense pyrrole reaction was obtained, and when reduced with fuming hydriodic acid at 150° it yielded glutamic acid, amongst other products. The sodium salt of the acid (1 mol.) when oxidised with chloramine-T (1 mol.) gave an aldehyde, $\text{C}_4\text{H}_6\text{O}_4$, which with *p*-nitrophenylhydrazine gave a characteristic osazone, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{C}(\text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2) \cdot \text{CH} \cdot \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 297—299°, giving a red ammonium salt. With potassium cyanate, β -hydroxyglutamic acid yielded a uramido-acid, which when heated with acids gave a very soluble hydantoin. The acid gave derivatives

with phenylcarbimide and β -naphthalenesulphonyl chloride, which were not well defined. It also gave characteristic colour reactions with various phenols and concentrated sulphuric acid.

The peptide mixture, extracted by the butyl alcohol from the products of hydrolysis of the caseinogen, was separated from proline, and obviously consisted of a number of different compounds. A tyrosine-containing peptide was isolated, but not identified, and also a peptide, which was shown to be *d-isoleucyl-d-valine anhydride* [isopropyl-sec.-butyldiketopiperazine],



m. p. 310—312°, $[\alpha]_D^{20}$ -42.0° to -43.5°.

W. G.

Formation, by Oxidation, of Organic Substances, of an Intermediate Substance spontaneously producing Carbamide.

R. FOSSE (*Compt. rend.*, 1919, 168, 320—322).—The author shows that whereas, by oxidation with potassium permanganate, substances such as casein and amino-acids give only a small yield of carbamide, if the oxidised solution is subsequently heated with aqueous ammonium chloride, a very much greater yield of carbamide is obtained. Similarly, if substances such as glycerol, carbohydrates, or formaldehyde are oxidised with potassium permanganate in the presence of ammonia, the yield of carbamide is practically negligible, but if the products are heated with aqueous ammonium chloride, a considerable yield of carbamide is obtained.

W. G.

The Action of Chlorine on Hydrazine, Hydroxylamine, and Carbamide.

C. T. DOWELL (*J. Amer. Chem. Soc.*, 1919, 41, 124—125).—When a large excess of chlorine is allowed to react with hydrazine and hydroxylamine in contact with carbon tetrachloride, evidence is obtained showing the formation of nitrogen trichloride, since on separating the carbon tetrachloride and treating it with a solution of potassium iodide, nitrogen is evolved. The author has confirmed the observations of Chattaway on the properties of dichlorocarbamide, in that when kept its solution is decomposed, giving as one of the products nitrogen trichloride. Chattaway considered that in the course of this decomposition carbon dioxide and monochloroamine were formed, the latter giving ammonia and nitrogen trichloride. The author, however, has tested the solution for monochloroamine by Raschig's test with ammonia and benzaldehyde, whereby, owing to the formation of hydrazine, the insoluble benzalazine should be produced. This is not the case, and no evidence of monochloroamine is obtained. It is suggested that the nitrogen trichloride may be formed by the action of chlorine, which may also be a decomposition product of dichlorocarbamide.

J. F. B.

Coal. AMÉ PICTET (*Ann. Chim.*, 1918, [ix], 10, 249—330).—A more detailed account of work already published (compare A., 1911, i, 850; 1913, i, 1315; 1914, i, 155; 1915, i, 512; 1916, i, 800; 1917, i, 515).

W. G.

Halogenation. XVIII. Direct Iodination by means of Iodine and Nitric Acid. RASIK LAL DATTA and NIHAR RANJAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1919, **41**, 292—295).—In continuation of the investigations on iodination by nitric acid (A., 1917, i, 332), it is found that the reaction takes place readily in the case of aromatic acids and aromatic haloid derivatives. Thus, iodobenzene gives a good yield of *p*-di-iodobenzene. Although a small proportion of trinitrophenol is formed as a result of the hydrolysis of iodobenzene and simultaneous nitration in presence of nitric acid (*loc. cit.*), it is not possible to prepare trinitrophenol catalytically by using a small quantity of iodine with continued addition of benzene and nitric acid, since iodobenzene is quite stable under these conditions, any excess of iodine yielding *p*-di-iodobenzene, and any excess of nitric acid, *p*-iodonitrobenzene. The latter is, however, formed by the prolonged action of iodine and nitric acid on benzene, since *p*-di-iodobenzene is decomposed by nitric acid, giving *p*-iodonitrobenzene,* a good yield of which may be rapidly prepared by this method of exhaustive iodination of benzene with repeated additions of iodine and nitric acid; the water accumulating on account of the decomposition of nitric acid must be removed from time to time.

On iodination with the required quantity of iodine and nitric acid, iodobenzene gives *p*-di-iodobenzene; chlorobenzene gives *p*-chloriodobenzene, and bromobenzene, *p*-bromiodobenzene. *p*-Chloro- and *p*-bromo-toluenes give *p*-chloro- and *p*-bromo-benzoic acids respectively, the methyl groups being oxidised to carboxyl and no entry of iodine taking place. From benzoic acid, *m*-iodobenzoic acid was obtained, and from *o*-phthalic acid, 4-iodo-*o*-phthalic acid. Phenylacetic acid gives *p*-iodophenylacetic acid and cinnamic acid, *p*-iodocinnamic acid. Salicylic acid yields trinitrophenol quantitatively, the carboxyl group being detached, and complex hydroxy-acids, such as tannin, give a small quantity of trinitrophenol; the latter is frequently obtained in traces on iodination of the aromatic acids.

T. H. P.

Meta-substituted Aromatic Selenium Compounds. FRANK LEE PYMAN (T., 1919, **115**, 166—175).

Preparation of Monomethylaniline. PERCY FARADAY FRANKLAND, FREDERICK CHALLENGER, and NOEL ALBERT NICHOLLS (T., 1919, **115**, 198—205).

Preparation of "Metol" (*N*-Methyl-*p*-aminophenol Sulphate). ROLLA N. HARGER (*J. Amer. Chem. Soc.*, 1919, **41**, 270—276).—In view of the comparative cheapness of quinol and also of methylamine when prepared by the methylation of ammonium chloride by means of formaldehyde (compare Werner, T., 1917, **111**, 844; Jones and Wheatley, A., 1918, i, 527), the author has made experiments on the preparation of "metol" by heating quinol and methylamine together under pressure. The

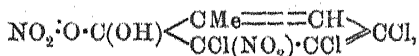
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results obtained show that a lower temperature, and consequently a very much lower pressure, and a much shorter period of heating than those given in the Merck specifications (A., 1913, i, 1057), are the conditions under which the reaction should be carried out; a yield of 73% is obtainable.

N-Methyl-*p*-aminophenol sulphate begins to char at 245° and has m. p. 250—260° (decomp.). It crystallises in microscopic, six-sided, prismatic needles with roof-like ends. Addition to its solution of mercuric acetate solution results in the gradual development of an intense purple coloration, which may probably serve for the colorimetric estimation of "metol." T. H. P.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylphenols. III. Nitric Acid Derivatives of Chlorinated *o*-Cresols. TH. ZINCKE and O. PREISS (*Annalen*, 1918, 417, 191—235. Compare Zincke and Pfaffendorf, A., 1912, i, 964; Zincke and Janney, A., 1913, i, 853).—The following new chloro-derivatives of *o*-cresol have been prepared. 4-Chloro-*o*-toluidine, by chlorination at 0° in glacial acetic and concentrated hydrochloric acids yields a *hexachloro-1-methylcyclohexene-2-one*, $C_7H_4OCl_6$, stout needles or prisms having a strong camphor-like odour, m. p. 105°, which is reduced in boiling alcoholic solution by tin alone to 3:4:5-trichloro-*o*-cresol, long needles, m. p. 77° (*acetyl* derivative, needles, m. p. 45°); if concentrated hydrochloric acid is also present, or if the reduction is effected by stannous chloride, tetrachloro-*o*-cresol is also produced. 3:5:6-Trichloro-*o*-cresol, needles, m. p. 62° (*benzoyl* derivative, needles, m. p. 110°), is prepared in a similar way from the keto-hexachloride obtained from 6-chloro-*o*-toluidine (Zincke and Pfaffendorf, *loc. cit.*). 4:5-Dichloro-*o*-cresol, needles, m. p. 101° (*benzoyl* derivative, needles, m. p. 80—81°), is obtained by leading the calculated quantity of chlorine into a chloroform solution of 4-chloro-*o*-cresol, needles, m. p. 73—74° (*benzoyl* derivative, leaflets, m. p. 53—54°), which is itself prepared from 4-chloro-*o*-toluidine.

3:4:5-Trichloro-*o*-cresolnitroquinotrol,



colourless, rhombic crystals, m. p. 105—106° (decomp.), obtained by adding 3:4:5-trichloro-*o*-cresol gradually to nitric acid, D 1.48, is converted into 3:4:6-trichloro-*p*-toluquinone by warm concentrated sulphuric acid, and is reduced (a) by stannous chloride, in cold dilute hydrochloric solution to 3:4:5-trichloro-*o*-cresol (a reduction of this kind cannot be effected with the corresponding tribromo-derivative, *loc. cit.*), (b) in methyl-alcoholic solution at 0° to 4:5-dichloro-3-nitro-*o*-cresol, yellow needles, m. p. 69° (*acetyl* derivative, rhombohedral crystals, m. p. 93—94°), and (c) in concentrated hydrochloric acid to 4:5-dichloro-3-amino-*o*-cresol, colourless leaflets, m. p. 161° (*hydrochloride*, leaflets; *diacetyl* derivative, needles, m. p. 194°; *triacetyl* derivative, leaflets, m. p. 126°), which is also obtained by the reduc-

tion of the preceding nitro-compound. The constitutions of these compounds are determined by the fact that the amino-compound can be converted into 4:5:6-trichloro-2:3-dihydroxytoluene.

By boiling with tetrachloroethane, 3:4:5-trichloro-*o*-cresol-nitroquinitrol is converted into 4:5-dichloro-*o*-toluquinone 2-nitrate, $\text{NO}_2 \cdot \text{O} \cdot \text{C}(\text{OH}) < \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{CO} - \text{CCl} \end{smallmatrix} > \text{CCl}$, yellow needles, m. p. 144° (decomp.), which is reduced by stannous chloride to 4:5-dichloro-2:3-dihydroxytoluene, needles, m. p. 107° (diacetyl derivative, needles, m. p. 112°). By chlorination in cold glacial acetic acid solution, 4:5-dichloro-2:3-dihydroxytoluene yields a keto-chloride, yellow prisms, m. p. $86-89^\circ$, which is reduced by stannous chloride to 4:5:6-trichloro-2:3-dihydroxytoluene. By oxidation with nitric acid (D 1.15) 4:5-dichloro-2:3-dihydroxytoluene yields 4:5-dichloro-2:3-toluquinone, dark red needles, m. p. 83° .

By treatment with nitric acid (D 1.48) 3:5:6-trichloro-*o*-cresol yields 3:5:6-trichloro-*o*-cresol-nitroquinitrol,

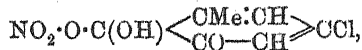


unstable, colourless crystals, m. p. 91° (decomp.). This differs from the 3:4:5-trichloro-isomeride in not being convertible into a dichlorotoluquinone nitrate, but resembles it in being converted into the trichlorotoluquinone by concentrated sulphuric acid. By boiling its solution in glacial acetic acid until nitrous fumes cease to be evolved and then reducing the cold solution with stannous chloride, 3:5:6-trichloro-*o*-cresol is regenerated. The nitroquinitrol is reduced by stannous chloride and dilute hydrochloric acid to 5:6-dichloro-3-amino-*o*-cresol, colourless needles (hydrochloride, needles; diacetyl derivative, needles, m. p. $204-205^\circ$), which is converted by chlorination in glacial acetic acid into a keto-chloride yielding 4:5:6-trichloro-2:3-dihydroxytoluene.

3:5-Dichloro-*o*-cresol-nitroquinitrol,



colourless needles, m. p. 109° (decomp.), obtained from 3:5-dichloro-*o*-cresol and nitric acid (D 1.48) is more stable than the two preceding nitroquinitrols, but it also decomposes slowly by keeping. It can be converted into 5-chloro-3-nitro-*o*-cresol, yellow needles, m. p. 107° (acetyl derivative, colourless needles, m. p. 88°), 5-chloro-3-amino-*o*-cresol, colourless needles, m. p. 107° (hydrochloride, leaflets; diacetyl derivative, needles, m. p. 196°), 4:5:6-trichloro-2:3-dihydroxytoluene, and 5-chloro-*o*-toluquinone 2-nitrate,



yellow crystals, m. p. $117-118^\circ$, by the methods described above. The last-mentioned compound is reduced by stannous chloride solution to 5-chloro-2:3-dihydroxytoluene, colourless needles, m. p. 89° (diacetyl derivative, needles, m. p. $65-66^\circ$), by stannous chloride

solution and concentrated hydrochloric acid to 5-chloro-6-amino-2:3-dihydroxytoluene, colourless leaflets, m. p. 150—160° (*hydrochloride*, needles; *triacetyl* derivative, needles, m. p. 183°; *tetraacetyl* derivative, leaflets, m. p. 135°), and by stannous chloride solution at 0° into 5-chloro-6-nitro-2:3-dihydroxytoluene, yellow needles and prisms, m. p. 135° (*diacetyl* derivative, colourless leaflets, m. p. 148°).

By chlorinating 5-chloro-6-amino-2:3-dihydroxytoluene hydrochloride in suspension in glacial acetic and concentrated hydrochloric acids a yellow keto-chloride is obtained, which by reduction in alcoholic solution with stannous chloride yields 5-chloro-2:3:6-trihydroxytoluene, colourless needles, m. p. 175°; this forms a *triacetyl* derivative, needles, m. p. 95°, and yields 5-chloro-2-hydroxy-p-toluquinone, pale red needles, m. p. 160°, by oxidation with nitric acid (D 1·15).

By treatment with nitric acid (D 1·48) at 0°, 4:5-dichloro-*o*-cresol yields 4:5-dichloro-3-nitro-*o*-cresol-nitroquinitrol,



colourless needles, m. p. 110° (decomp.), which yields 4:5-dichloro-*o*-toluquinone 2-nitrate (above) by boiling in tetrachloroethane solution and 4:5-dichloro-3-nitro-*o*-cresol by reduction with stannous chloride in methyl-alcoholic solution at 0°.

4-Chloro- and 6-chloro-*o*-cresols, by treatment with nitric acid, yield, not nitroquinitrols, but 4-chloro-3:5-dinitro-*o*-cresol, yellow needles, m. p. 146° (*acetyl* derivative, colourless needles, m. p. 109—110°), and 6-chloro-3:5-dinitro-*o*-cresol, yellow needles, m. p. 82—83° (*acetyl* derivative, colourless needles, m. p. 95°), respectively.

C. S.

Chlorotrihydroxytoluenes. TH. ZINCKE and GRETE SCHÜRMANN (*Annalen*, 1918, **417**, 236—254).—3-Chloro-6-nitro-*o*-cresol, colourless needles, m. p. 79° (*acetyl* derivative, leaflets, m. p. 84°), prepared by treating 6-nitro-*o*-cresol in chloroform solution with the calculated quantity of chlorine, is converted by nitric acid (D 1·48) at 0° into 3-chloro-5:6-dinitro-*o*-cresol, stout, faintly yellow needles or prisms, m. p. 134° (*acetyl* derivative, colourless needles, m. p. 136°), which in alcoholic solution is reduced by stannous chloride solution to 3-chloro-5:6-diamino-*o*-cresol, colourless needles (*triacetyl* derivative, colourless needles, m. p. 236°), the *hydrochloride* of which, stout needles, by chlorination in glacial acetic and concentrated hydrochloric acids yields 1:3:3:4:4-pentachloro-2:5:6-triketo-1-methylcyclohexane, $\text{CMeCl} < \begin{matrix} \text{CO} \cdot \text{CCl}_2 \\ \text{CO} - \text{CO} \end{matrix} > \text{CCl}_2$, yellow plates, m. p. 68°. This keto-chloride is reduced by stannous chloride solution to 3-chloro-2:5:6-trihydroxytoluene, m. p. 175°, which is identical with the substance obtained by Zincke and Preiss from 3:5-dichloro-*o*-cresol-nitroquinitrol (preceding abstract).

By methods similar to the preceding, the following substances

have been prepared, starting with 4-nitro-*o*-cresol; 3-chloro-4-nitro-*o*-cresol, faintly yellow needles or leaflets, m. p. 74° (acetyl derivative, colourless needles or leaflets, m. p. 59°); 3-chloro-4:5-dinitro-*o*-cresol, faintly yellow needles, m. p. 139° (acetyl derivative, colourless needles, m. p. 167°); 3-chloro-4:5-diamino-*o*-cresol, colourless needles (hydrochloride, colourless needles, triacetyl derivative, needles, m. p. 230° , azine from phenanthraquinone, $C_{21}H_{13}ON_2Cl$, brownish-yellow leaflets, m. p. 273°); 1:3:3:6:6-pentachloro-2:4:5-triketo-1-methylcyclohexane, $C_7H_3O_3Cl_5$, pale yellow plates and prisms, m. p. 78° ; and 3:6-dichloro-2:4:5-trihydroxytoluene, colourless needles, m. p. 155° (triacetyl derivative, needles, m. p. 151°). The last substance is oxidised by nitric acid (D 1.15), followed by acid, D 1.4, to 3:6-dichloro-4-hydroxy-*p*-toluquinone, red needles, m. p. 157° .

An alkaline solution of 3-chloro-4:5-diamino-*o*-cresol is oxidised by air to 3-chloro-4-amino-*p*-toluquinone-5-imide, $C_7H_7ON_2Cl$, red needles, m. p. 175 — 177° (decomp.; blackening at about 160°), which exhibits basic properties. 3-Chloro-4:5-diamino-*o*-cresol hydrochloride is oxidised by *N*-ferric chloride solution to 3-chloro-4-amino-*p*-toluquinone, dark red needles, m. p. about 142° , which is reduced by stannous chloride to 3-chloro-4-amino-2:5-dihydroxytoluene, colourless needles (hydrochloride, leaflets; triacetyl derivative, needles, m. p. 185°). C. S.

Organic Chemical Reagents. III. β -Phenylhydroxylamine and "Cupferron" (Ammonium Salt of Nitroso-phenylhydroxylamine). C. S. MARVEL and OLIVER KAMM. (*J. Amer. Chem. Soc.*, 1919, **41**, 276—282. Compare A., 1918, i, 482; this vol., i, 61).—The statement made by various authors that β -phenylhydroxylamine is obtainable in theoretical yield by the reduction of nitrobenzene by means of zinc dust is inaccurate. Directions are now given for the reduction of nitrobenzene in portions of 500 grams, a yield of the dry product amounting to 64% of the theoretical being obtainable.

For the preparation of "cupferron," dry β -phenylhydroxylamine is not required, and the conditions are given under which the moist product is treated in ethereal solution with ammonia and amyl nitrite so as to obtain "cupferron" in a yield 80—90% of that theoretically possible. Even with the present high prices of materials and labour, "cupferron" may be made in the laboratory, where the labour charge is an abnormally high proportion of the total expenses, at a cost considerably less than the pre-war price of the product. [See *J. Soc. Chem. Ind.*, 1919, April.] T. H. P.

The Identification of Acids. IV. Phenacyl Esters. J. B. RATHER and E. EMMET REID (*J. Amer. Chem. Soc.*, 1919, **41**, 75—83).—In previous communications (A., 1917, i, 334, 559) the use of *p*-nitrobenzyl bromide for the identification of organic acids by the melting points of their *p*-nitrobenzyl esters was described. It is now shown that phenacyl bromide (ω -bromoacetophenone) may

be employed in a precisely similar manner and that in some cases the phenacyl esters of the acid are still more definitely characteristic than the *p*-nitrobenzyl esters. Phenacyl bromide is prepared by bromination of acetophenone in glacial acetic acid solution. The acid is neutralised with rather less than the theoretical quantity of sodium carbonate, and, working with 0.05 gram-mol. of the reagents, this quantity is dissolved in 5 c.c. of water, 1 gram of phenacyl bromide is added and then 10 c.c. of 95 per cent. alcohol. The ester is obtained after boiling for one hour with monobasic, two hours with dibasic, and three hours with tribasic acids. It is recrystallised from dilute alcohol until the melting point is constant. The following phenacyl esters have been characterised: acetate, m. p. 40°; aconitate, m. p. 90°; *o*-aminobenzoate, m. p. 181—182°; benzoate, m. p. 118.5°; *p*-bromobenzoate, m. p. 87°; cinnamate, m. p. 140.5°; citraconate, m. p. 108.5°; citrate, m. p. 104°; *m*-cresotate, m. p. 116.5°; *o*-cresotate, m. p. 138.5°; *p*-cresotate, m. p. 145.5°; fumarate, m. p. 197.5°; glutarate, m. p. 104.5°; itaconate, m. p. 79.5°; lactate, m. p. 96°; malate, m. p. 106°; maleate, m. p. 119°; *p*-nitrobenzoate, m. p. 128.4°; palmitate, m. p. 52.5°; pyrotartrate, m. p. 101.5°; saccharate, m. p. 120°; salicylate, m. p. 110°; stearate, m. p. 64°; succinate, m. p. 148°; tartrate, m. p. 130°.

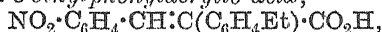
J. F. B.

Pschorr's Phenanthrene Synthesis. II. FRITZ MAYER and FRANK ALBERT ENGLISH (*Annalen*, 1918, 417, 60—92. Compare Mayer and Balle, A., 1914, i, 536).—As the result of the experiments here recorded, it appears impossible to synthesise 8-, 5-, or 7-ethylphenanthrene by any of the methods at present known.

o-Ethylbenzyl alcohol, $C_6H_4Et \cdot CH_2 \cdot OH$, b. p. 229°, obtained by the electrolytic reduction of *o*-ethylbenzoic acid at a lead cathode in dilute sulphuric acid solution, is converted by cold saturated hydrobromic acid into *o*-ethylbenzyl bromide, colourless crystals, m. p. 34°, b. p. 225°/751 mm. The latter is converted by alcoholic sodium cyanide into *o*-ethylphenylacetone nitrile, $C_6H_4Et \cdot CH_2 \cdot CN$, b. p. 257—258°/752 mm., which is hydrolysed by heating with 35% potassium hydroxide solution (2 mols.) and 30% hydrogen peroxide (3 mols.), yielding *o*-ethylphenylacetic acid, m. p. 83.5° (ethyl ester, a colourless, odourless oil). Attempts to reduce this acid to *o*-ethylbenzaldehyde, a colourless, odourless liquid, b. p. 210°/753 mm., by the methods of Mettler and Piria gave unsuccessful or unsatisfactory results, but the aldehyde is obtained in 67% yield by oxidising *o*-ethylbenzyl alcohol with potassium dichromate and 10% sulphuric acid, and in 33.6% yield by heating *o*-ethylbenzyl bromide with hexamethylenetetramine in 60% alcoholic solution. Further experiments were undertaken to ascertain the influence of negative substituents in the benzene nucleus on the Sommelet reaction. *o*-Nitrobenzyl chloride and hexamethylenetetramine, boiled in 60% alcoholic solution for four hours, yielded, in addition to a small quantity of a substance, $C_{23}H_{15}O_7N_5$, m. p. 153.5°, a substance, m. p. 112°, which is regarded as *tri-o*-nitro-

benzyltrimethylenetriamine, $\text{NX} \begin{smallmatrix} \text{CH}_2 \cdot \text{NX} \\ \text{CH}_2 \cdot \text{NX} \end{smallmatrix} \text{CH}_2$ [where X is $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2$], since its molecular weight corresponds with this formula, and it yields formaldehyde and *o*-nitrobenzylamine hydrochloride by hydrolysis with boiling concentrated hydrochloric acid. In a similar manner, *p*-nitrobenzyl chloride and hexamethylenetetramine yield *tri-p-nitrobenzyltrimethylenetriamine*, m. p. 161° , whilst *o*- and *p*-chlorobenzyl chlorides yield *o*- and *p*-chlorobenzaldehydes respectively.

The attempt to condense *o*-ethylbenzaldehyde and sodium *o*-nitrophenylacetate by means of acetic anhydride and zinc chloride at 120° in an atmosphere of carbon dioxide yielded a very small quantity of a *substance*, $\text{C}_9\text{H}_9\text{O}_3\text{N}$, colourless crystals, m. p. 183.5° . A similar attempt to condense *o*-nitrobenzaldehyde and potassium *o*-ethylphenylacetate for two days at 100° yielded β -*o*-nitrophenyl- α -*o*-ethylphenylacrylic acid,



m. p. 194° . By reduction with ferrous sulphate and aqueous ammonia, it yields the corresponding *amino-acid*, colourless crystals, m. p. $178-179^\circ$, but the attempt to convert this into 8-ethylphenanthrenecarboxylic acid by shaking its diazotised solution with copper powder or by boiling with water yielded in the first case a non-crystallisable product, and in the second case β -*o*-hydroxyphenyl- α -*o*-ethylphenylacrylic acid, $\text{C}_{17}\text{H}_{16}\text{O}_3$, m. p. 205° .

The starting material in the attempt to synthesise 5- or 7-ethylphenanthrene is acetophenone, which by successive nitration and reduction yields *m*-aminoacetophenone. The latter is converted by hydrazine hydrate at 160° into a mixture of the *azine*, $\text{C}_{16}\text{H}_{18}\text{N}_4$, m. p. 147° , and the *hydrazone*, $\text{C}_8\text{H}_{11}\text{N}_3$, m. p. 98° , which is reduced by Wolff's sodium ethoxide method at 160° to *m*-ethylaniline; Staudinger and Kupfer's method of reduction with hydrazine hydrate at 210° , however, gives a greatly improved yield. *m*-Ethylaniline is converted by Sandmeyer's method into *m*-ethylbenzonitrile, $\text{C}_6\text{H}_4\text{Et} \cdot \text{CN}$, b. p. $116-117^\circ/25$ mm. This is hydrolysed to *m*-ethylbenzoic acid, from which, by methods similar to those used in the ortho-series above, are obtained in succession *m*-ethylbenzyl alcohol, b. p. $227^\circ/758$ mm., *m*-ethylbenzyl bromide, *m*-ethylphenylacetoneitrile, $\text{C}_6\text{H}_4\text{Et} \cdot \text{CH}_2 \cdot \text{CN}$, b. p. $250-254^\circ/761$ mm., *m*-ethylphenylacetic acid, m. p. $62-64^\circ$, and *m*-ethylbenzaldehyde, b. p. 212° .

Potassium *m*-ethylphenylacetate and *o*-nitrobenzaldehyde, condensed together by means of zinc chloride and acetic anhydride at 120° in an atmosphere of carbon dioxide, yield β -*o*-nitrophenyl- α -*m*-ethylphenylacrylic acid, m. p. 138° . This is reduced by ferrous sulphate and ammonia to the *amino-acid*, $\text{C}_{17}\text{H}_{17}\text{O}_2\text{N}$, m. p. $150-150.5^\circ$, the diazotised solution of which yields by boiling or by shaking with copper powder a mixture of β -*o*-hydroxyphenyl- α -*m*-ethylphenylacrylic acid, m. p. 203° (decomp.), and an ethylphenanthrenecarboxylic acid, $\text{C}_{17}\text{H}_{14}\text{O}_2$, m. p. $147-149^\circ$, which is

probably 5-ethylphenanthrene-9-carboxylic acid. Attempts to convert the latter into ethylphenanthrene by heating under ordinary or reduced pressure were unsuccessful. C. S.

Hydroxy-carbonyl Compounds. I. New Synthesis of Hydroxy-aldehydes. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 89—94).—A rapid current of hydrogen chloride is passed for several hours into dry ether containing resorcinol, cyanogen bromide, and anhydrous zinc chloride. The crystals of the intermediate product, which contains chlorine, but not bromine, are collected and dissolved in cold water, and the solution, after being washed with ether, is boiled for twenty minutes. The 2:4-dihydroxybenzaldehyde, which is thus produced in good yield, is extracted with ether. It appears to be formed by the reactions: (i) $\text{CBrN} + \text{HCl} = \text{CHBr}\cdot\text{NCl}$; (ii) $\text{CHBr}\cdot\text{NCl} + \text{C}_6\text{H}_4(\text{OH})_2 = \text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{NCl} + \text{HBr}$; (iii) $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{NCl} \xrightarrow{\text{H}_2\text{O}} \text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CHO}$.

Phloroglucinol reacts in a similar manner.

C. S.

Phenols Insoluble in Alkali Hydroxides. ROGER ADAMS (*J. Amer. Chem. Soc.*, 1919, 41, 247—270).—Investigation has been made of the phenylhydrazones of the *o*-hydroxyaldehydes and ketones in order to determine the structure characteristic of such compounds of this type as are insoluble in alkali hydroxides. The results show that the introduction of a methyl group, or, in general, of a group containing carbon, into either the phenolic ring or the side-chain of one of these phenylhydrazones is accompanied by marked depression of the solubility of the compound in 10% aqueous sodium hydroxide. A bromine atom produces a less effect, which is the more noticeable with substitution in the side-chain. When a nitro-group is introduced into the phenolic ring in the ortho- or para-position to the hydroxyl group, the solubility in alkali is increased, and a nitro-group in the para-position in the phenylhydrazone residue has the same effect. This result is regarded as due to the possibility of the rearrangement of nitrophenols and of *p*-nitrophenylhydrazones to aci-nitro-compounds, which are readily soluble in alkali. Where there is no tendency to form aci-nitro-compounds, as with the *m*- and *o*-nitrophenylhydrazones, the nitro-group has the same effect as other groups and increases the insolubility in alkali hydroxides. No compound with a nitro-group in the meta-position to the hydroxyl was prepared, but such a compound should show diminished solubility in alkali. Comparison of the phenylhydrazones of *p*-homosalicylaldehyde and pænonol with the corresponding hydrazones, the former being insoluble and the latter soluble in alkali hydroxides, shows that a large group like phenyl in the hydrazone residue is absolutely necessary for the compound to show insolubility in alkali. The marked effect of a methyl or phenyl group attached to the carbon atom carrying the phenylhydrazone residue, as compared with a hydrogen atom, is shown by the perfect solubility of the azines of *p*-homosalicyl-

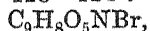
aldehyde and β -naphthaldehyde in cold alkali hydroxide solution and the insolubility of the azines of pæonol and 2-hydroxy-5-methylbenzophenone in boiling alkali. Finally, a substituent group attached to the iminic nitrogen has a decided effect in reducing the solubility in alkali hydroxides.

The various explanations which have been advanced to account for the insolubility of these phenolic compounds in alkali hydroxide solution are discussed and shown to be unsatisfactory, and the author regards this behaviour as due to the fact that such compounds are very weak acids and highly insoluble in water. Any insoluble, slightly hydrolysed acid would be expected to behave similarly, and the introduction into its molecule of a positive or negative atom or group will have a result determined by two distinct effects: first, the insolubility in water due to the increased size of the whole molecule, this leading to increased insolubility in alkali hydroxide, and, secondly, an increase or a decrease in the acidity of the whole molecule, depending on the nature and position of the group introduced.

Pæonol phenylhydrazone is soluble in hot alkali solution; the *hydrazone*, $C_9H_{12}O_2N_2$, white plates, quickly turning yellow on exposure, m. p. $73-75^\circ$, dissolves in cold alkali hydroxide; the *azine*, $C_{13}H_{20}O_4N_2$, lemon-yellow crystals, m. p. $226-227^\circ$, is insoluble in boiling alkali hydroxide; the 2:4:6-*tribromophenylhydrazone*, $C_{15}H_{12}O_2N_2Br_3$, white needles, m. p. 162° , is insoluble in boiling alkali hydroxide.

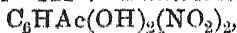
Bromopæonol, $C_9H_9O_3Br$, has m. p. 169° (Brüll and Friedländer, A., 1897, i, 221, gave 171°); its *phenylhydrazone*, $C_{15}H_{15}O_2N_2Br$, slender, yellow needles, m. p. $172.5-173.5^\circ$, its *p-bromophenylhydrazone*, dull yellow, monoclinic plates, m. p. 189.5° , and its 2:4:6-*tribromophenylhydrazone*, white needles, m. p. $169-171^\circ$, are insoluble in boiling alkali hydroxide. Its *methyl ether*, $C_{10}H_{11}O_3Br$, forms white needles, m. p. $139-140^\circ$; neither this *methyl ether* nor that of pæonol itself yields a phenylhydrazone in the ordinary way.

ω -*Tribromobromopæonol*, $OH \cdot C_6H_2Br(OMe) \cdot CO \cdot CBr_3$, forms lemon-yellow needles, m. p. $123-124^\circ$. *Bromonitropæonol*,

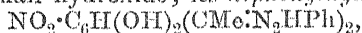


forms long, hairy needles, m. p. $112-114^\circ$; its *phenylhydrazone*, $C_{15}H_{14}O_4N_3Br$, forms saffron-coloured crystals, m. p. $204.5-205.5^\circ$, and dissolves gradually in cold, readily in warm alkali. *Nitropæonol*, $C_9H_9O_5N$, forms white needles, m. p. 155° ; its *phenylhydrazone*, $C_{15}H_{15}O_4N_3$, orange needles, m. p. $215.5-216.5^\circ$, is soluble slightly in cold, readily in warm alkali hydroxide; its *methyl ether*, $C_{10}H_{11}O_5N$, forms slender, white needles, m. p. 131° , gradually turning yellowish-red. *Aminopæonol*, $C_9H_{11}O_3N$, forms greenish-yellow, monoclinic prisms, m. p. $112-113^\circ$; its *platinichloride* was prepared and analysed.

Dinitroacetylresacetophenone, $C_6HAc(OH)(OAc)(NO_2)_2$, forms white plates, m. p. $121-122^\circ$. *Dinitroresacetophenone*,



forms pale yellow crystals resembling fine sand, m. p. 166—167°, and its *phenylhydrazone*, $C_{14}H_{12}O_6N_4$, reddish-brown crystals, darkening at 238° and decomposing at 242.5°. *Acetylaminoresacetophenone*, $C_6H_3Ac(OH)_2 \cdot NHAc$, forms white needles, m. p. 254°. *Nitrosodiaceetophenone*, $C_6HAc_2(OH)_2 \cdot NO_2$, forms white needles, m. p. 231°; its *phenylhydrazone*, $C_{16}H_{15}O_5N_3$, pale yellow powder, darkening at 220° and decomposing sharply at 235°, is soluble in cold alkali hydroxide; its *diphenylhydrazone*,

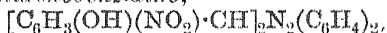


massive, lemon-yellow needles, becoming orange-red and decomposing at 273°, dissolves slightly in cold and readily in warm alkali hydroxide.

Bromoresodiacetophenone, $C_{10}H_9O_4Br$, forms white plates, m. p. 205°.

Salicylaldehyde *o*-tolylhydrazone dissolves in alkali hydroxide only in the hot; the 2:4:6-tribromophenylhydrazone, white needles, m. p. 100°, dissolves gradually, with decomposition, in boiling alkali hydroxide.

Di-5-nitrosalicylidenebenzidine,



forms red crystals not melting below 275° and dissolves partly in boiling alkali hydroxide. *Di-3-nitrosalicylidenebenzidine* forms bright red crystals not melting below 275°, and is somewhat more soluble in boiling alkali hydroxide than the 5-isomeride.

p-Homosalicylaldehydephenylhydrazone is soluble in hot alkali hydroxide; the *hydrazone*, $C_8H_{10}ON_2$, white powder, m. p. 72—74°, dissolves in cold alkali hydroxide.

Bromo-p-homosalicylaldehyde, $C_8H_7O_2Br$, forms yellow crystals shrinking at 63°, m. p. 65°, and its *phenylhydrazone*, $C_{14}H_{13}ON_2Br$, dirty yellow crystals, m. p. 140—141°, soluble in hot alkali hydroxide.

5-Methyl-2-hydroxybenzophenoneazine, $[C_6H_3Me(OH) \cdot CPh]_2N_2$, forms lemon-yellow crystals, m. p. 259—260°, and is insoluble in boiling sodium hydroxide solution.

T. H. P.

Pinacolin Transformations. IV. Ring Changes produced by the Elimination of Water from Alicyclic Alcohols.

HANS MEERWEIN (*Annalen*, 1918, 417, 255—277. Compare A., 1914, i, 850).—In connexion with the previous investigation (*loc. cit.*), 1-methyl-1- α -hydroxyethylcyclopentane has been synthesised and also submitted to the dehydrating action of zinc chloride, and the constitution of the resulting hydrocarbon has been determined; it is 1:2-dimethyl- Δ^1 -cyclohexene, and the reaction is one of the smoothest changes known of a cyclopentane into a cyclohexane derivative.

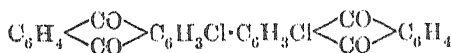
[With CL. FLEISCHHAUER].—The reaction between magnesium and 1-chloro-1-methylcyclopentane in ether at 5—10°, preferably in the absence of air, and treatment of the product with carbon dioxide and subsequently with ice-water and dilute sulphuric acid, lead to the formation of 1-methylcyclopentane-1-carboxylic acid,

the acid chloride of which reacts with magnesium methyl iodide in ether at -15° to form, after the usual treatment, 1-methyl-1-cyclopentyl methyl ketone, $C_5H_8Me \cdot COMe$, b. p. $48.4^{\circ}/10$ mm., in good yield, the semicarbazone of which forms colourless needles, m. p. $143-144^{\circ}$. By reduction with sodium and moist ether, the ketone yields 1-methyl-1- α -hydroxyethylcyclopentane, $C_5H_8Me \cdot CHMe \cdot OH$, b. p. $67.6^{\circ}/10.5$ mm., together with the corresponding pinacone, $C_{10}H_{20}O_2$, colourless prisms, m. p. $89-90^{\circ}$, the former of which yields only 1:2-dimethyl- Δ^1 -cyclohexene by heating with zinc chloride at $180-190^{\circ}$.

The acid chloride of 1:2:2:3-tetramethylcyclopentane-1-carboxylic acid reacts with zinc methyl or, better, magnesium methyl iodide in ether to form, ultimately, 1:2:2:3-tetramethyl-1-cyclopentyl methyl ketone, $C_{11}H_{20}O$, b. p. $101-102^{\circ}/18$ mm. (semicarbazone, m. p. 232°), which is reduced by sodium and moist ether to 1:2:2:3-tetramethyl-1- α -hydroxyethylcyclopentane, $C_{11}H_{22}O$, b. p. $108-109^{\circ}/15$ mm. The alcohol appears to be a mixture of two stereoisomeric forms, since it partly solidifies, the solid form having m. p. $70-71^{\circ}$, D_4^{20} 0.9113 (supercooled), n_D^{20} 1.46322. By heating with zinc chloride, the alcohol yields a mixture of 1:2:3:3:4-pentamethyl- Δ^1 -cyclohexene (chief product) and 1:2:2-trimethyl-3-isopropyl- Δ^3 -cyclopentene, the constitutions of which are deduced from the nature of the products of the decomposition of the ozonides. C. S.

mesoNaphthodianthrones. ALFRED ECKERT and RUDOLF TOMASCHER (*Monatsh.*, 1918, **39**, 839-864).—The authors have endeavoured to synthesise derivatives of mesonaphthodianthrone in a manner which leaves no doubt as to their constitution. For this purpose the method of Scholl, Mansfield, and Potschiwuscheg (A., 1910, i, 494) as modified by Ullmann and Minajeff (A., 1912, i, 366) has been applied to certain $\alpha\alpha'$ -dichloroanthraquinones; of these only the 1:4-derivative reacts with copper powder, the 1:5- and 1:8-dichloro- and the 1:4:5:8-tetrachloro-products remaining unattacked. The procedure of Meyer, Bondy, and Eckert (A., 1913, i, 62) is not applicable to halogenated anthraquinones, since the halogen is partly eliminated during reduction with zinc and alkali. A more successful process consists in converting the anthranols into the corresponding dihydrodianthrones, enolisation of the latter (enolisation by alkali occurs less readily with derivatives than with the parent substance and the products are considerably less stable), and oxidation of the material so formed to the dianthrone; the latter is converted into the corresponding mesonaphthodianthrone when exposed to light. In cases in which formation of the mesonaphthalene ring cannot occur by simple elimination of hydrogen, a peculiar phenomenon is observed; when dissolved in nitrobenzene or xylene, the substance is unchanged after protracted illumination, whilst in concentrated sulphuric acid solution elimination of two atoms of hydrogen and two of chlorine slowly occurs.

4:4'-Dichloro-1:1'-dianthraquinonyl,



pale yellow crystals, is reduced by copper powder and concentrated sulphuric acid to 4:4'-dichloromesobenzdianthrone, yellowish-brown needles, which under the action of light pass into 4:4'-dichloromesonaphthdianthrone, $\text{CO} \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{Cl} \\ \diagdown \text{C}_6\text{H}_3 \end{array} \text{C}=\text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_2\text{Cl} \\ \diagdown \text{C}_6\text{H}_3 \end{array} \text{CO}$, small, yellow needles.

1(or 4)-Chloroanthrone, yellow needles, m. p. 106°, obtained by the reduction of 1-chloroanthraquinone by aluminium bronze and sulphuric acid, is oxidised by ferric chloride to 4:4'-dichlorodihydrodianthrone, colourless crystals which darken without melting at 270°. The enolic form of this substance is an unstable, green powder, which is readily converted by persulphate into 4:4'-dichlorodianthrone, greenish-yellow crystals, from which 4:4'-dichloromesonaphthdianthrone is obtained by exposure to light.

1:4-Dichloroanthrone, yellow needles, m. p. 136—138°, 1:4:1':4'-tetrachlorodihydrodianthrone, colourless crystals, m. p. 250° (decomp.), and 1:4:1':4'-tetrachlorodianthrone, yellow plates, are prepared by a similar series of reactions; the latter substance loses two atoms of hydrogen and two of chlorine when its solution in concentrated sulphuric acid is exposed to light, but the product obtained did not give sharp analytical results.

1:5-Dichloroanthrone yields 1:5:1':5'-tetrachlorodihydrodianthrone, colourless crystals, and 1:5:1':5'(or 4:8')-tetrachlorodianthrone, yellow platelets; the corresponding mesonaphthdianthrone could not be obtained in the pure state. Similarly, 1:8-dichloroanthrone, yellow needles, m. p. 115°, 4:5:4':5'-tetrachlorodihydrodianthrone, colourless crystals which remain unchanged up to 280°, 4:5:4':5'-tetrachlorodianthrone, pale yellow crystals, and 4:5:4':5'-tetrachloromesonaphthdianthrone, small, yellow needles, were prepared.

3:3'-Dibromomesobenzdianthrone forms a reddish-yellow, crystalline powder which is converted by light into 3:3'-dibromomesonaphthdianthrone, pale yellow powder.

Starting from 1:3-dichloroanthraquinone (Meyer and Zahn, A., 1913, i, 455), the constitution of which is now definitely established by its conversion into 1:3-diphenoxyanthraquinone (Ullmann and Eiser, A., 1916, i, 823), the following series of substances is obtained: 3:3'-dichloro-1:1'-dianthraquinonyl, greenish-yellow needles, 3:3'-dichloromesobenzdianthrone, yellowish-brown needles, and 3:3'-dichloromesonaphthdianthrone, small, yellow needles. Attempts to prepare the substance last named from 2-chloroanthraquinone led to a different product through the following stages: 2-chloroanthrone, yellow needles, m. p. 115—120°, which are readily oxidised; 3:3'(3:2')-dichlorodihydrodianthrone, silvery, crystalline powder, m. p. 240° (decomp.); 3:3'(3:2')-dichlorodianthranol, greenish-yellow, crystalline powder; dichlorodianthrone, yellow,

crystalline powder, in which the position of the chlorine atoms is not decided; and (3:6')-dichloromesonaphthodianthrone, small, yellow needles. H. W.

Constitutions of the Fenchene Hydrocarbons. WALTER QVIST (*Annalen*, 1918, 417, 278—324).—The author has examined the fenchenes obtained by different methods and having b. p.'s below 150°. He shows that Aschan was right in stating that β -pinolene (*cyclofenchene*) occurs in the fenchene fraction, b. p. below 150°, obtained from fenchyl chloride. Kondakov and Lutschinin's hydrocarbon (A., 1907, i, 713) is not β -pinolene, but is identical with the author's *isofenchylene*.

When *DL*-fenchyl alcohol is heated with aluminium phosphate at 210° or with potassium hydrogen sulphate at 200°, the hydrocarbons obtained contained *d*- β -fenchene and a little *l*- α -fenchene in the fraction of high b. p. (152—155°) and *d*-*cyclofenchene* and *i*-*isofenchylene* in the fractions, b. p. 141—143° and 143—145°. *d*-*cyclofenchene* is also obtained by heating *DL*-fenchyl xanthate at 230°, *l*- α -fenchene also being produced. Since both these hydrocarbons yield the same hydrochloride, which yields *l*- α -fenchene by heating with *o*-toluidine, the xanthate method is an excellent means of preparing pure *l*- α -fenchene.

Very pure *d*- β -fenchene (*dibromide*, $C_{10}H_{16}Br_2$, crystals, m. p. 81—82°, $[\alpha]_D^{25} -31.2^\circ$ in ethyl acetate) is obtained by heating *l*-isofenchyl chloride with *o*-toluidine. By the xanthate method *l*-isofenchyl alcohol yields *l*-isofenchylene.

β -Pinolene yields two dibromides, namely, *l*- and *i*- α -fenchene dibromides. This proves that Aschan's β -pinolene and the author's tricyclic hydrocarbon obtained from *DL*-fenchyl alcohol are identical, with the difference, however, that the latter is feebly dextro-rotatory *d*-*cyclofenchene* whilst the former is a mixture of *l*-*cyclofenchene* and *dl*-*cyclofenchene*.

The reduction of *d*- α -fenchene dibromide by zinc dust and 75% alcohol at 55° yields fenchane and *l*- α -fenchene. As these two hydrocarbons contain different skeletons, no conclusions can be drawn as to the constitution of the α -fenchene dibromide. C. S.

Phenylurethanes of Terpene Alcohols and Phenols. F. WEERHUIZEN (*Pharm. Weekblad*, 1919, 56, 299—301).—The terpene alcohol or phenol is dissolved in petroleum (distilling between 170° and 200°). The requisite quantity of phenylcarbimide is added and the solution boiled. On cooling, the phenylurethane crystallises out in quantitative yield and is recrystallised from benzene (80—100°). The phenylurethanes of the following substances were prepared: *o*-, *m*-, *p*-cresol (m. p. 141°, 121—122°, 111—112° respectively), thymol (m. p. 106—107°), menthol (m. p. 111—112°), borneol (m. p. 137—138°), eugenol (m. p. 95°).

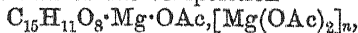
The method may be used for the separation of camphor and borneol. The former is unacted on and remains in solution; the latter separates out as bornylphenylurethane. W. S. M.

Constituents of Resins. IV. β -Dammar-resin. ALOIS ZINKE and ERNA UNTERKREUTER (*Monatsh.*, 1918, **39**, 865—869).—Analyses and determinations of molecular weight show the hydrocarbon portion of β -dammar-resin (compare Dulk, *Jahrb. pr. Chem.*, 1848, **45**, 16; Tschirch and Glimmann, A., 1896, i, 164) to have the composition $C_{30}H_{48}$; it melts indefinitely at 195° after softening from 165° , and possibly represents a mixture of hydrocarbons. Attempts have been made to prepare derivatives of it by oxidation, action of nitrous acid, and action of ethereal hydrogen chloride, but definite products have not been isolated. H. W.

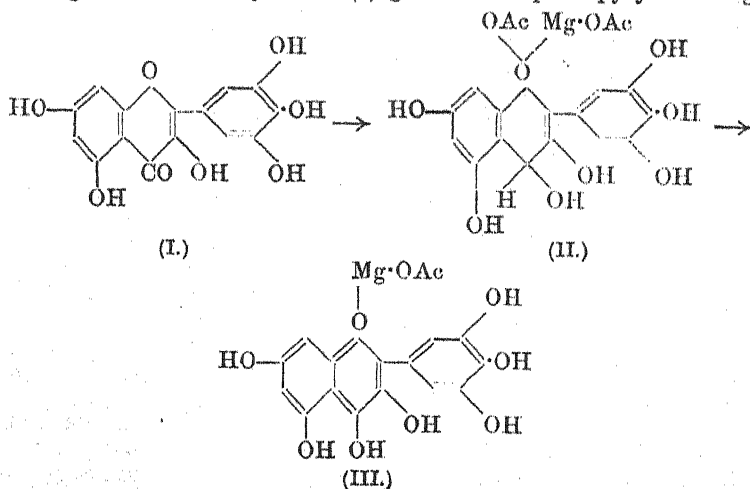
Biochemical Synthesis, by means of Emulsin, of α -Naphthylcarbinyll- β -glucoside. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 323—324).—When emulsin acts on an acetone solution of dextrose and α -naphthylcarbinol, α -naphthylcarbinyll- β -glucoside, long needles, m. p. 156 — 157° (corr.), $[\alpha]_D -71.02^\circ$, is obtained, which is readily hydrolysed by emulsin or by dilute sulphuric acid. W. G.

Anthocyanins : Colour Variation in Anthocyanins. KEITA SHIBATA, YUJI SHIBATA, and ITIZO KASIWAGI (*J. Amer. Chem. Soc.*, 1919, **41**, 208—220).—For the reduction of compounds of the flavone and flavanol series, organic acids may be used in conjunction with zinc or magnesium in place of inorganic acids. With monobasic acids deep green to bluish-green pigments are mostly obtained, the tints varying slightly according to the reagents employed. Some of these pigments were isolated and their properties examined.

When reduced with magnesium and glacial acetic acid, myricetin gives green compounds of the composition

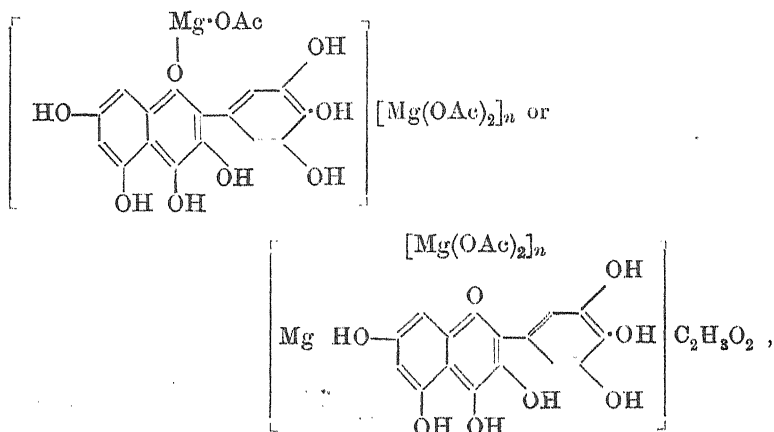


n being 2 or 4; the myricetin (I) gives first a phenopyrylium ring



(II), the organo-metallic compound (III) then resulting by elimination of acetic acid from the ring.

As the acetates of the bivalent metals often tend to form complex compounds, it was to be expected that addition of magnesium acetate would take place, giving:



according to Werner's co-ordination theory.

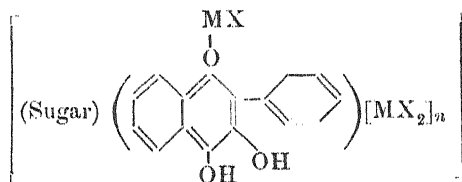
Similarly, myricitrin, a rhamnoside of myricetin, gives with the same reagents a deep blue product co-ordinated with four molecules of magnesium acetate.

The above green or blue pigments are soluble in water as well as in alcohol, giving neutral solutions with the same colours, but the addition of dilute acid (hydrochloric) to the solutions changes the colour to red, the $\text{Mg} \cdot \text{OAc}$ group of the green pigment (III) being replaced by a chlorine atom in the red oxonium salt. This explains why Willstätter and others have always obtained red pigments by reduction of the yellow pigments. Even with inorganic acids green or blue pigments are formed under certain conditions, treatment of myricetin with alcoholic hydrochloric acid yielding a deep green pigment in the molecule of which the position of the $\text{Mg} \cdot \text{OAc}$ group (III) is occupied by $\cdot \text{MgCl}$; here addition of magnesium chloride does not take place, probably because of its smaller tendency to form complex salts. The compound dissolves in water and alcohol, giving neutral solutions of the original colour.

That all the above compounds have deep colours or, in other words, that their absorption bands are displaced far towards the red end of the spectrum, is attributed on the one hand to the fact that the phenylpyrylium ring of the green or blue pigments has one more hydroxyl group than that of the oxonium salts, and on the other to the fact that magnesium forms the complexes with its auxiliary valence, which together play the rôle of bathochromism. In the case of the reduced glucoside, flavanol, one of the hydroxyl groups is replaced by a sugar molecule, which shifts the absorption

band hypsochromatically, that is, towards the violet end of the spectrum.

From these results and those of experiments on the pigments of many flowers, the following explanation of the various flower colours is based. The metal organic or complex compounds of reduced flavanol glucosides (annexed formula) are the most important factor in the production of flower colours. The "blue" anthocyanins are the complex compounds of reduced flavanol glucosides, which possess several hydroxyl groups belonging to the flavanol nucleus besides those of sugar molecules, and the metal with which they are



co-ordinated is probably calcium or magnesium, as salts of these metals are always present in the plant cells. The "violet," "violet-red," or "red" pigments are either the analogous metallic complex compounds of flavanol glucosides, which contain fewer of the auxochrome hydroxyl groups, or a mixture of the blue pigments and their products of decomposition by excess of acids, that is, Willstätter's red oxonium salts.

This theory is confirmed by the behaviour of the natural anthocyanin solutions towards the salts of alkaline earth and heavy metals, addition of the latter to alcoholic extracts of various flowers always acting bathochromatically.

Experimental details are given.

T. H. P.

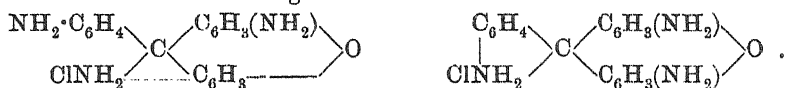
A New Yellow Dye and Light Filters made from It.

C. E. K. MEES and H. T. CLARKE (*Brit. J. Photo.*, 1919, 66, 48).—The new dye is the *glucosazone* formed by the condensation of dextrose with *p*-hydrazinobenzoic acid; it gives a very soluble sodium salt.

W. G.

Composition of Pyrocresoles and their Relationship to Coal Tar Constituents. FRIEDRICH RUSZIG (*Zeitsch. angew. Chem.*, 1919, 32, [i], 37—40).—The so-called isomeric pyrocresoles, isolated by Schwarz (A., 1883, 204; 1884, 79) from the residue of the distillation of crude phenol, have the same composition, $\text{C}_{15}\text{H}_{10}\text{O}$, and properties as the compounds prepared by Gladstone and Tribe (T., 1889, 55, 51) by the decomposition of the aluminium *o*-, *m*-, and *p*-tolyloxides. They have been identified as dimethylxanthen, whilst the homologous compound, $\text{C}_{13}\text{H}_{10}\text{O}$, is xanthen, produced by the decomposition of aluminium phenoxide in accordance with the equation $2\text{Al}(\text{O}\cdot\text{C}_6\text{H}_5)_3 = (\text{C}_6\text{H}_5)_2\text{O} + \text{C}_{13}\text{H}_{10}\text{O} + \text{C}_6\text{H}_5\cdot\text{OH} + \text{CH}_4 + \text{C}_4 + \text{Al}_2\text{O}_3$. From aluminium *m*-tolyloxide, two isomeric dimethylxanthen, corresponding with Schwarz's α - and β -pyrocresoles, were prepared, but the third isomeric modification was not found.

Aluminium *p*-tolylloxide yielded symmetrical *p*-dimethylxanthen (m. p. 168°), whilst from aluminium *o*-tolylloxide the 4:5-dimethylxanthen was obtained. The liquids of high boiling point which separate at the end of the distillation of aluminium phenoxide have the composition $C_{19}H_{14}O$, and appear to be formed from xanthen, as follows: $C_{13}H_{10}O + C_6H_5 \cdot OH = C_{19}H_{14}O + H_2O$. On dissolving this compound in nitric acid and adding water, an amorphous, yellow compound is precipitated. By reducing this with zinc and acetic acid, and precipitating the base with ammonia, a brown colouring matter is obtained. Its hydrochloride is soluble in water and acts as a direct brown dye for wool and silk. This dye, for which the name xanthen-brown is suggested, is an inner ester of magenta and has a constitution corresponding with one of the following formulæ:



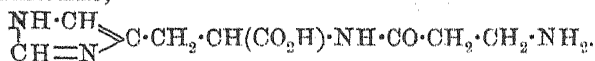
Analogous compounds obtained in the distillation of aluminium tolyloxides had the composition of tolyldimethylxanthenes and also yielded xanthen-browns, and similar compounds were obtained from the anthracene oils of coal tar, which probably consist, in part, of triphenylmethane derivatives, and, in particular, of phenyl- and diphenyl-xanthenes. [See also *J. Soc. Chem. Ind.*, 1919, April.]

C. A. M.

Synthesis of Aminoflavones, of Flavone-azo- β -naphthol Dyes and of other Flavone Derivatives. MARSTON TAYLOR BOGERT and JOSEPH K. MARCUS (*J. Amer. Chem. Soc.*, 1919, **41**, 83—107).—Flavone was prepared by a modification of Ruhemann's method (A., 1913, i, 891), using smaller quantities of aluminium chloride and benzene. Nitration in the cold by nitric and sulphuric acids in glacial acetic acid solution yielded mixtures which were separated into two fractions, consisting of 2'- and 3'-nitroflavones and of 3'- and 4'-nitroflavones. These were converted by reduction with stannous chloride into the aminoflavones, the three isomerides being separated and purified by taking advantage of their different basicities and solubilities. 2'-Aminoflavone crystallises from hot acetone in silky, pale yellow needles, m. p. 149.5—150.5° (corr.); 3'-aminoflavone crystallises from pyridine or xylene in lemon-yellow, straight needles, m. p. 156—157° (corr.), and 4'-aminoflavone crystallises from the same solvents in long, golden-yellow needles, m. p. 234—236° (corr.). From the three aminoflavones, the corresponding hydroxyflavones were prepared by means of the diazonium salts, and were decomposed by sodium ethoxide and alcohol into *o*-hydroxyacetophenone and *o*-, *m*-, and *p*-hydroxybenzoic acids, owing to the rupture of the pyrone ring at the double bond. 2'-Hydroxyflavone forms lustrous, colourless plates, m. p. 249—250° (corr.). The three aminoflavones have been diazotised and coupled with β -naphthol to form flavoneazo- β -naphthols, m. p. 265—266.5°, 257°, and 274—275° (corr.) respectively, giving

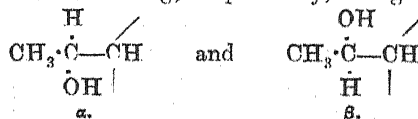
orange to red shades on silk and wool, extremely fast to light and alkalis. Other compounds obtained are 2'-*acetoxyflavone*, m. p. 88·5—89° (corr.), 2'-*diacetylaminoflavone*, m. p. 186·5—187·5° (corr.), 3'-*diacetylaminoflavone*, m. p. 231—232° (corr.), 4'-*diacetylaminoflavone*, m. p. 246—248° (corr.), β -*phenoxy- β -phenylpropionic acid*, m. p. 150—151° (corr.), the barium salt of a disulphonic derivative of the latter acid, and *methyl β -bromo- β -phenylpropionate*, m. p. 37·5—38·5° (corr.). It is noted that whereas all the hydroxyflavones are colourless, all the aminoflavones are yellow, thus indicating the more powerful auxochromic effect of the amino-group in this series; also 4'-aminoflavone possesses the remarkable property of fluorescence only in neutral solvents which contain the hydroxyl group. J. F. B.

Carnosine, Constitution and Synthesis. GEORGE BARGER and FRANK TUTIN (*Biochem. J.*, 1918, 12, 402—407).—2:4:5-Trinitrotoluene condenses with amino-acids when boiled in dilute alcoholic solution, the amino-acid becoming attached to the benzene ring by its amino-group, which replaces the reactive nitro-group in position 5. This reaction does not occur with imino-groups, but does take place with the free amino-groups of peptides. The condensation product of 2:4:5-trinitrotoluene with carnosine on hydrolysis yields dinitrotolyl- β -alanine, thus proving carnosine to be β -alanylhistidine,



For the synthesis of carnosine, β -*nitropropionyl chloride*, b. p. 123°/10 mm., was condensed with histidine methyl ester, and the resulting very unstable product was at once reduced by stannous chloride and dilute hydrochloric acid, and the carnosine isolated as its copper salt. W. G.

The α - and β -Hydroxydihydrocinchonines and their Rôle in the Production of certain Isomerides of Cinchonine. E. LÉGER (*Compt. rend.*, 1919, 168, 404—407).—The so-called β -hydroxycinchonine, like its α -isomeride (compare A., 1918, i, 304), when acted on by 50% sulphuric acid gives a mixture of cinchonigine, cinchoniline, and *apocinchonine*. The ratio of cinchonigine to cinchoniline obtained from the β -isomeride is practically the inverse of that obtained from the α -isomeride, but if the strength of the acid is increased to 70% and the heating prolonged to twenty-four hours, the proportions of these two bases are almost the same from each isomeride. From this, the author concludes that β -hydroxycinchonine, like the α -isomeride (*loc. cit.*), is a product of the addition of the elements of water to cinchonine, the two isomerides containing, respectively, the groupings



W. G.

Nicotinic Acid Derivatives. II. Guvacine and *iso*Guvacine.

E. WINTERSTEIN and A. B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1918, **104**, 48—53. Compare A., 1918, i, 35).—In view of recent publications on the same subject (Hess and Liebbbrandt, A., 1918, i, 401; Hess, *ibid.*, 403; Freudenberg, *ibid.*, 403), the authors submit a short account of their experiments, fuller details being promised in a later paper. They are led to the conclusion that guvacine is in all probability Δ^3 -tetrahydronicotinic acid (contrast Trier, A., 1913, i, 803), whereas *isoguvacine* is a simple derivative of pyrrole.

The following details are given. Guvacine crystallises in prisms, m. p. 293—295°, is neutral to litmus, and optically inactive. The hydrochloride, platinichloride, and aurichloride have m. p.'s 312°, 233°, and 195—197° respectively; nitrosoguvacine forms needles, m. p. 167°. Reduction of guvacine with hydrogen in the presence of platinum leads to the formation of dihydroguvacine, m. p. 252° (hydrochloride, m. p. 237°; platinichloride, m. p. 233—235°; aurichloride, prismatic needles, m. p. 193—195°; mercurichloride, m. p. 230—231°), which is shown to be identical with hexahydronicotinic acid. Methylation of guvacine leads to the formation of *N*-dimethylguvacine, m. p. 225° (?) [hydrochloride, m. p. 256—258°; platinichloride, m. p. 253°; aurichloride, m. p. 224—226°; picrate, m. p. 224—225°; mercurichloride, m. p. 174—176°], which is found to be identical in all respects with the arecadinemethylbetaine described by Willstätter (A., 1897, i, 385).

*iso*Guvacine has m. p. 220°, is faintly acid to litmus, and is optically inactive. The hydrochloride, m. p. 231° (decomp.), platinichloride, m. p. 235° (decomp.), and aurichloride, m. p. 198—200°, are described. When the base is heated with zinc dust, an intense odour of pyrrole is observed, and a pine shaving dipped in concentrated hydrochloric acid is coloured intensely red. *iso*Guvacine is slowly reduced by hydrogen in the presence of platinum, but the hydrochloride of the new base is not uniform: the platinichloride has m. p. 225°. *iso*Guvacine forms a dimethyl derivative, the platinichloride of which has m. p. 252°. H. W.

Ring Formation with Elimination of a Nitro-group.

S. REICH and (MLLE.) V. NICOLAEVA (*Helv. Chim. Acta*, 1919, **2**, 84—88).—The reaction examined by Reich with Gaigallian (A., 1917, i, 595) and with Turkus (*ibid.*, i, 585) has been further studied. Whilst the phenylhydrazones of ethyl 2:4-dinitrophenylglyoxylate, of 2:6-dinitrobenzaldehyde, and of 2-chloro- or 2-bromo-6-nitrobenzaldehyde yield *iso*indazole derivatives with the loss of a nitro-group under the influence of alkali, 2:4-dinitrobenzaldehydephenylhydrazone remains unchanged by similar treatment. To test the theory that this difference in behaviour is sterically due to the accumulation of atoms and atomic groups round the aldehydic carbon atom, 2:4-dinitroacetophenonephenylhydrazone, reddish-brown needles, m. p. 165—166°, has been pre-

pared from 2:4-dinitroacetophenone, an oil which is obtained by hydrolysing its oxime, yellow prisms, m. p. 124°, with warm 15% hydrochloric acid. The oxime is obtained in 20—30% yield by the action of amyl nitrite and sodium ethoxide on 2:4-dinitroethylbenzene, the main product of this reaction, however, being 5-nitro-2-methylindoxazen, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CMe} \\ \text{O} \end{smallmatrix} \text{N}$, yellow crystals, m. p. 114°.

In accordance with the theory above, 2:4-dinitroacetophenone-phenylhydrazone is converted by treatment with cold aqueous-alcoholic sodium hydroxide into 6-nitro-1-phenyl-3-methylisindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NPh} \\ \text{CMe} \end{smallmatrix} \text{N}$, yellow spangles, m. p. 139—140°.

C. S.

Thienylquinolinecarboxylic Acid. MAX HARTMANN and ERNST WYBERT (*Helv. Chim. Acta*, 1919, 2, 60—63).—2-2'-Thienylquinoline-4-carboxylic acid, $\text{C}_4\text{H}_2\text{S} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{CO}_2\text{H}$, yellow leaflets, m. p. 211°, is obtained by heating 2-thienyl methyl ketone, isatin, 28% potassium hydroxide solution and alcohol on the water-bath for three hours and acidifying the cooled solution with acetic acid. By repeated recrystallisation the acid is obtained in colourless crystals having the same m. p., but by solution in alkali and reprecipitation by acid the yellow modification is regenerated. The ethyl ester, colourless needles, has m. p. 83°. The salts of the acid are extremely soluble in water, forming solutions having a neutral reaction.

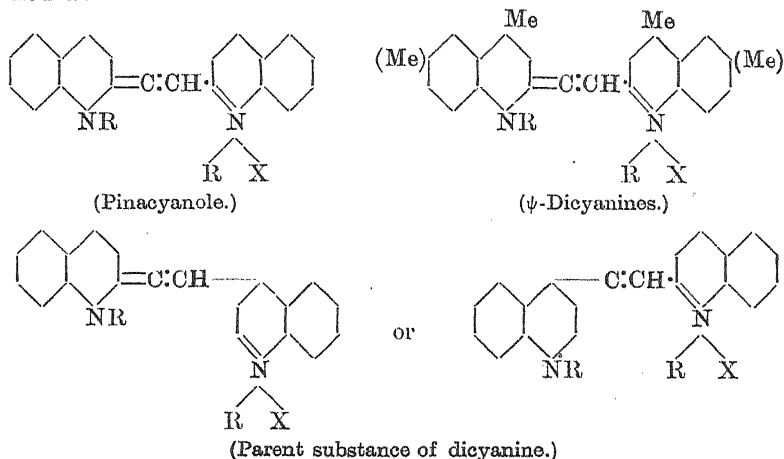
The acid resembles, but exceeds, 2-phenylquinoline-4-carboxylic acid in its antiphlogistic and analgesic action. When fed to an animal or when injected in the form of a soluble salt into the blood system it produces in the animal a violet-red colour and the urine acquires the colour of concentrated potassium permanganate solution. The colouring matter, which is very persistent and appears in almost all the internal organs, can be isolated from the urine and is obtained in small crystals (C=56.51; H=4.57; N=5.41; S=7.31%. Mol. wt. in freezing naphthalene=2207). The substance has pronounced acid properties, exhibits none of the colour reactions typical of thiophen, and cannot be produced from the thienylquinolinecarboxylic acid in the laboratory.

C. S.

Nitro-, Arylazo-, and Amino-glyoxalines. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (*T.*, 1919, 115, 217—260).

Quinocyanines (Pinacyanoles, Dicyanines). OTTO FISCHER (*J. pr. Chem.*, 1918, [ii], 98, 204—232).—Little has hitherto been known of the blue cyanines which have been put on the market under the names pinacyanole chloride, dicyanine bromide, and ψ -dicyanine iodide, and are stated to be the best sensitisers in photography. Considerable light is now thrown on the conditions of their formation. For the production of pinacyanoles and of their homologues, the ψ -dicyanines obtained from 2:4-di- and 2:4:6-trimethylquinoline alkyl iodides, two quinoline molecules are necessary,

each containing a methyl group in position 2, by means of which the two molecules are united together. For the production of dicyanines are necessary two quinoline molecules, one containing a methyl group in position 2 and the other a methyl group in position 4:



In the formulæ $R = \text{Me}$ or Et and $X = \text{halogen}$.

The chromophore of the *isocyanines* (for example, ethyl-red) contains two, that of the *pinacyanoles* three, and that of the *dicyanines* four double linkings, which accounts for the deepening of the colours from violet-blue through blue to greenish-blue.

[With (Frl.) C. BAUER, (Frl.) P. MERKEL, and G. SCHEIBE].—The simplest pinacyanole, quinaldine-blue (formula given above), was prepared (Farbwerke vorm. Meister, Lucius & Brüning, D.R.-P. 172118) by boiling an alcoholic solution of quinaldine ethiodide, with or without quinoline ethiodide, with aqueous sodium hydroxide in the presence of formaldehyde. At first it was believed that two different blue pinacyanoles were formed, but it is now shown that only one is obtained, the quinoline ethiodide taking no part in the reaction. It is also shown that the presence of formaldehyde (or, as stated in the patent claim, of glyoxylic acid, iodoform or chloroform), although advantageous, is not essential, provided air or other oxidising agent, such as potassium ferricyanide or ammonium persulphate, is present. It is true that in the case of quinoline derivatives unsubstituted in position 4 the latter methods result chiefly in the production of *isocyanines*, but when position 4 is occupied by a methyl or phenyl group the product is chiefly the pinacyanole.

In addition to the iodide (quinaldine-blue), m. p. about $276\text{--}278^\circ$ (decomp.), the bromide, m. p. about $274\text{--}275^\circ$ (decomp.), chloride, m. p. about 263° (decomp.), picrate, decomp. about $250\text{--}260^\circ$, *platinichloride*, *aurichloride*, and *mercurichloride* are described, and also the additive compounds of the iodide and bromide respec-

tively with bromine. Attempts to find evidence of the presence of a ruptured ring by testing for the presence of a secondary amine gave negative results. By oxidation with an excess of alkaline potassium ferricyanide solution, pinacyanole chloride yields 1-ethylquinolone.

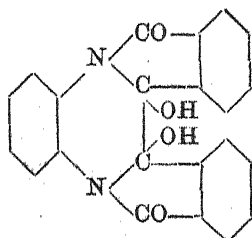
Many attempts were made to convert ethyl-red and its homologues into pinacyanoles by means of formaldehyde, but the violet-blue substances obtained showed no similarity at all to the pinacyanoles.

By boiling an alcoholic solution of 2:4-dimethylquinoline ethiodide and potassium hydroxide ($\frac{1}{2}$ mol.) in a current of air a mixture of several colouring matters is produced, from which the ψ -dicyanine iodide, $C_{26}H_{27}N_2I$ (formula above), and the dicyanine iodide (formula above) have been isolated in the form of the corresponding bromides. When 4-phenyl-2-methylquinoline methiodide is similarly treated in methyl-alcoholic solution, no dicyanine is formed, but the ψ -dicyanine, 4:4'-diphenylpinacyanole iodide, $C_{34}H_{27}N_2I$, crystals containing CH_4O (*picrate*, almost black, crystalline powder), is obtained. A similar result is obtained in the case of 4-phenyl-2:6-dimethylquinoline methiodide, but 2:4:6-trimethylquinoline ethiodide, which again contains a methyl group in position 4, yields both the ψ -dicyanine iodide (chief product) and the dicyanine iodide. The former, $C_{28}H_{31}N_2I$, green prisms containing C_2H_6O , forms blue solutions which appear reddish-violet in thin layers (*picrate*, dark green leaflets), whilst the latter, $C_{28}H_{31}N_2I$, forms green needles (*picrate*, greenish-black needles; *bromide*, green needles).

The various classes of cyanines are differentiated by their absorption spectra.

C. S.

Condensation of Aromatic *Ortho*Diamines with Phthalic Anhydride. HANS LIEB (*Monatsh.*, 1918, 39, 873—895).—It has been shown by Edlbacher that diphtalyl-*o*-phenylenediamine, $C_{26}H_{14}N_2[(CO)_2C_6H_4]_2$, can be reduced by zinc dust and acetic acid to a substance, m. p. 275—277° (decomp.), which, at its melting point, passes into a red, crystalline product, $C_{22}H_{12}O_2N_2$, m. p. 278°. The present communication deals with the constitution of these substances, the elucidation of which in the first case is greatly hampered by the difficulty of eliminating solvent of crystallisation. The



author, however, considers the material to be 1:2:3:4-dibenzoylene-1:2:3:4-tetrahydro-2:3-dihydroxyquinoxaline (annexed formula), whilst the substance, $C_{22}H_{12}O_2N_2$, is 1:2:3:4-dibenzoylene-1:4-dihydroquinoxaline. Similar substances may be obtained from phthalic anhydride and 1:2-naphthalenediamine.

Diphtalyl-o-phenylenediamine, m. p. 297°, is obtained in 45% yield by heating a mixture of phthalic anhydride and

o-phenylenediamine, and is reduced to 1:2:3:4-*dibenzoylene*-2:3-*dihydroxy*-1:2:3:4-*tetrahydroquinoxaline*, which separates from glacial acetic acid (+ $1\text{C}_2\text{H}_4\text{O}_2$) in yellow prisms, and from aqueous alcohol (+ H_2O) in indefinite, crystalline aggregates. The m. p. is not sharp, the substance becoming red at above 260° and yielding an intensely red, molten mass at $274\text{--}278^\circ$ with brisk evolution of gas. Attempts to prepare an acetyl or benzoyl derivative, an oxime or a hydrazone were unsuccessful, but the action of methyl sulphate yielded a *monomethyl ether*, $\text{C}_{23}\text{H}_{16}\text{O}_4\text{N}_2\cdot\text{H}_2\text{O}$, m. p. 190° , after softening and evolving gas from 170° . 1:2:3:4-*Dibenzoylene*-1:4-*dihydroquinoxaline* crystallises in intensely red needles, m. p. 278° ; it slowly dissolves in concentrated alcoholic potassium hydroxide, and the solution, on acidification, yields a substance which at $270\text{--}273^\circ$ is reconverted into the red product, but which, in spite of its close similarity, is not identical with the original material.

Attempts to prepare the red substance from biphtalyl and *o*-phenylenediamine were not successful, the product obtained being *o*-phenylenedibenziminazole (annexed formula), colourless needles, m. p. 425° (decomp.), which was also prepared by condensing dihydrodiphtalyl with *o*-phenylenediamine or from the amine and phthalic anhydride at 290° in a sealed tube. The corresponding *acetyl* and *benzoyl* derivatives have m. p.'s $198\text{--}199^\circ$ after softening at 195° and $229\text{--}230^\circ$ after softening at 225° respectively.

The following derivatives have been obtained from 1:2-naphthylenediamine: *diphtalyl*-1:2-*naphthylenediamine*, rhombohedra or hexagonal prisms, m. p. 282° , which on reduction gives the *product*, $\text{C}_{26}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. $280\text{--}284^\circ$, with evolution of gas and formation of a red mass, and 1:2:3:4-*dibenzoylene*-1:4-*dihydro*-5:6-(7:8)-*benzquinoxaline*, red needles, m. p. $323\text{--}324^\circ$, after sintering at 321° . During the preparation of the first-named substance, 1:2-*naphthylenebenziminazole*-*o*-carboxylic acid, leaflets, m. p. $304\text{--}305^\circ$, is obtained as by-product; this is converted by acetic anhydride into *benzoylenenaphthiminazole*, $\text{C}_{18}\text{H}_{10}\text{ON}_2$, orange-yellow needles, m. p. 213° .

H. W.

Proteins. I. Preparation of Ovalbumin Solutions of well-defined Composition, and the Analytical Methods used. S. P. L. SÖRENSEN [with MARGRETHE HÖYRUP] (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 1—11, 12—67; *Zeitsch. physiol. Chem.*, 1918, **103**, 1—14, 15—79).—The crystals of ovalbumin are prepared by the Hopkins and Pinkus' method, and after being recrystallised six times are free from ash, conalbumin, and mucoid. By means of a dialysing apparatus described in detail, solutions of ovalbumin may be completely freed from sulphate and almost entirely freed from ammonia. The content of water, ammonia,

and sulphuric acid in the crystals of ovalbumin is derived by the application of the "principle of proportionality," according to which, if an ovalbumin solution is precipitated by ammonium sulphate and the crystalline precipitate subsequently filtered off, and if weighed parts of the filtrate as well as of the precipitate with the adherent mother liquor are analysed, it is possible from the results of the analyses to draw certain conclusions regarding the composition of the precipitate on the presumption that the mother liquor surrounding the precipitate has the same composition as the filtrate.

H. W. B.

Proteins. II. Capacity of Ovalbumin to Combine with Acids or Bases. S. P. L. SÖRENSEN [with MARGRETHE HÖYRUP, JENNY HEMPEL, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 68—163; *Zeitsch. physiol. Chem.*, 1918, **103**, 104—210).—From theoretical considerations it is possible to calculate the hydrogen-ion concentration in an aqueous salt solution containing an excess of an acid or base corresponding with the salt. By an extension of the method, formulæ are deduced which permit of the calculation of the hydrogen-ion concentration of solutions of ampholytes containing small amounts of free acid, account being taken of the dissociation of the ampholyte into hydrogen- and ampholyte-anions and into hydroxyl and ampholyte cations respectively. The effect of the addition of salts is then considered, and it is found that at hydrogen-ion concentrations which are not in the neighbourhood of the isoelectric point of the ampholyte the capacity to combine with acids is (a) independent of the concentration of the ampholyte, (b) increased by increasing the concentration of the salt, (c) positive at hydrogen-ion concentrations superior to that corresponding with the isoelectric point of the ampholyte, and negative (that is, the ampholyte is combined with surplus base) at hydrogen-ion concentrations inferior to it. After testing the accuracy of these formulæ by application to solutions of amino-acids and salts, they are applied to solutions of ovalbumin, and it is found that the capacity of the ovalbumin to combine with acids is independent of the concentration of the ovalbumin at hydrogen-ion concentrations which are greater or smaller than that corresponding with the isoelectric point of the ovalbumin provided the concentration of ammonium sulphate is constant. It is further increased by increasing the concentration of the ammonium sulphate. At the isoelectric point the capacity of the ovalbumin to combine with acids is to some extent dependent on its concentration. By reference to a curve, the slight excess of sulphuric acid present in a solution of ovalbumin containing ammonium sulphate may be calculated, and also the method of its distribution between the two phases of the ovalbumin solution, namely, the dispersed phase consisting of hydrated ovalbumin and the external phase of ammonium sulphate and water. From these considerations the isoelectric point of ovalbumin is found to be at about 15.74×10^{-6} H. W. B.

Proteins. III. Composition and Properties of Ovalbumin Separated in Crystalline Form by means of Ammonium Sulphate. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 164—212; *Zeitsch. physiol. Chem.*, 1918, **103**, 211—266. Compare preceding abstracts).—By the application of the principle of proportionality, it is found that the crystals of ovalbumin contain water to the extent of about 0.22 gram of water per 1 gram of ovalbumin. The amount of water present is independent of the conditions of crystallisation (time and temperature of crystallisation, concentrations of ammonium sulphate, protein, and hydrogen ions). It is similarly found that if the crystallisation takes place at a hydrogen-ion concentration of about 13×10^{-6} , the crystals contain neither surplus sulphuric acid nor ammonia; at higher hydrogen-ion concentrations, the crystals contain surplus sulphuric acid, at lower concentrations they contain surplus ammonia. A consideration of the character of the crystallisation process leads the authors to the conclusion that the crystallisation of ovalbumin is simply the crystallisation of a supersaturated solution of a substance crystallising slowly and with difficulty.

In a postscript, it is announced that successful crystallisations of ovalbumin have been obtained by means of a mixture of ammonium and diammonium phosphates instead of ammonium sulphate. The crystals so obtained closely resemble those prepared in the usual manner.

H. W. B.

Proteins. IV. State of Equilibrium between Crystallised Ovalbumin and Surrounding Mother Liquor, and the Applicability of Gibbs's Phase Rule to such Systems. S. P. L. SÖRENSEN and MARGRETHE HÖYRUP (*Compt. rend. trav. Lab. Carlsberg*, 1917, **12**, 213—261; *Zeitsch. physiol. Chem.*, 1918, **103**, 267—323. Compare preceding abstracts).—The relations existing between crystallised ovalbumin and the surrounding mother liquor are in conformity with those associated with a heterogeneous system containing one solid phase, hydrated ovalbumin, and three other components, water, ammonia, and sulphuric acid. The system in all essential features is conformable to Gibbs' phase rule. At the equilibrium point, the content of ovalbumin in the mother liquor is smaller as the concentration of ammonium sulphate increases. The hydrogen-ion concentration at which the concentration of ovalbumin in the mother liquor is at a minimum corresponds with $p_{\text{H}} = 4.58$, and seems to be independent of the concentration of ammonium sulphate and the temperature of crystallisation. Similarly, the optimum temperature is at about 20° ; but little variation is observed between the limits of 12° and 29° .

The velocity of crystallisation increases with the concentration of ammonium sulphate, with the initial concentration of protein, and with the temperature of crystallisation.

H. W. B.

Proteins. V. Osmotic Pressure of Ovalbumin Solutions.

S. P. L. SÖRENSEN [with J. A. CHRISTIANSEN, MARGRETHE HÖYRUP, S. GOLDSCHMIDT, and S. PALITZSCH] (*Compt. rend. trav. Lab. Carlsberg*, 1918, **12**, 262—372. Compare preceding abstracts).—The osmometer used consists essentially of a collodion cap serving the purpose of a semi-permeable membrane and containing the ovalbumin solution employed as inner liquid, the outer liquid being an ammonium sulphate solution in diffusion equilibrium with the dispersion medium of the inner liquid. The osmotic pressure is measured by determination of the counter-pressure required to be exerted on the surface of the inner liquid to prevent a migration of the liquids through the membrane. On increasing the concentration of ammonium sulphate, the osmotic pressure of the ovalbumin is depressed. This result is explained by assuming that the increased amount of ammonium sulphate favours the condensation of two or more hydrated ovalbumin particles into a single particle by means of the bivalent sulphate group.

The osmotic pressure does not undergo any material alteration when the hydrogen-ion concentration is varied between 40×10^{-6} and 100×10^{-6} ; at higher concentrations, the pressure increases very slowly with the hydrogen-ion concentration, whilst at concentrations inferior to 40×10^{-6} , it increases rapidly as the concentration decreases. These results are also accounted for by the assumption of a condensation process promoted by the sulphate group.

From the various results which have been so far obtained, the number of nitrogen atoms contained in a single non-condensed ovalbumin particle is estimated at approximately 380; hence the molecular weight of anhydrous ovalbumin appears to be about 34,000. Taking into account the results obtained indicating the amount of sulphuric acid contained in the crystallised ovalbumin, the albumin crystals seem to consist normally of two albumin particles bound together by three molecules of sulphuric acid.

H. W. B.

"Proteins of Cow's Colostrum. I. The Relation between the Euglobulin and ψ -Globulin of Cow's Colostrum.

HAROLD WARD DUDLEY and HERBERT ERNEST WOODMAN (*Biochem. J.*, 1918, **12**, 339—351).—The authors have studied the optical properties of euglobulin and ψ -globulin of cow's colostrum when dissolved in $N/2$ - and $N/4$ -sodium hydroxide, and also the optical properties of the amino-acids derived from the hydrolysis of "racemised" colostrum euglobulin and ψ -globulin. The results obtained support the view that these two substances are structurally identical in so far as the protein portion of the molecule is concerned.

W. G.

Some Metallic Compounds of Hæmatoporphyrin. JOHN ALEXANDER MILROY (*Biochem. J.*, 1918, **12**, 318—338).—The author has prepared the compounds of hæmatoporphyrin with zinc, cadmium, nickel, cobalt, iron, copper, tin, and lead, has described their absorption spectra, and determined their resistance to the

action of mineral acids and the resistance of the absorption bands of the pigments to dilution.

The stannous compound may be prepared directly from blood or hæmatin, and on this is based a delicate test for the detection of traces of blood pigment. The stained tissue, where blood is suspected, is boiled with a little glacial acetic acid in a small test-tube. To the boiling solution, three drops of 2*M*-stannous chloride solution are added, and the solution is boiled for one minute. After filtering off the precipitate formed, the absorption bands of acid hæmatoporphyrin can easily be seen. A small quantity of solid sodium acetate is then added, and the solution is again boiled. The fluid, which is now bright red, is cooled and filtered, and the filtrate shows the two characteristic absorption bands of the stannous derivative. A method is given for extracting the blood pigment with phenol prior to this examination, and it is claimed that, by this means, it is possible to detect blood pigment at a dilution of $10^{-6} \times M/5$. W. G.

Pyrrrole Reaction of the true Nucleic Acids. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1918, 104, 1).—A pine shaving moistened with concentrated hydrochloric acid is coloured carmine-red by the vapours obtained by heating a dry mixture of sodium nucleate and ammonium chloride; the reaction is not shown by sodium nucleate alone. Since furan derivatives are readily converted into derivatives of pyrrole by dry distillation with ammonium salts, the author regards the reaction as a confirmation of his theory (A., 1914, i, 1098; 1918, i, 85) that the carbohydrate group of the true nucleic acids belongs to the furan type. H. W.

Mutarotation of Gelatin and its Significance in Gelatinisation. C. R. SMITH (*J. Amer. Chem. Soc.*, 1919, 41, 135—150).—In solution, gelatin exhibits mutarotation, and a study of the influence of changes of temperature on this mutarotation shows that in aqueous solution two forms of gelatin probably exist, one, termed the sol form *A*, stable above 33—35°, and the other, called the gel form *B*, stable below 15°. Between these temperatures, the two forms exist in equilibrium, and the mutarotation appears to be due to the transformation of the one form into the other by a reaction reversible with the temperature. This reaction is apparently bimolecular, that is, of the type to be expected if two molecular or equivalent weights of form *A* combine to form one molecular weight of form *B*. The relationship between the percentage quantities of the two forms when equilibrium is established at any given temperature between 17° and 33° seems to be represented by the equation $(a-x)^2/x=K$, in which *a* is the difference (about 1.2) between the rotations produced by 1 gram of gelatin per 100 c.c. in a tube 100 mm. long at 33—35° and at 17°, *x* is the difference between the rotations at 33—35° and at the given temperature, and *K* is a constant. Increase in lævorotation, indicating increasing formation of the gel form *B*, follows closely increase in viscosity.

A definite proportion of form *B* is necessary to form a jelly of standard viscosity, and this proportion, slightly increased as concentration increases, produces the standard viscosity in gelatin solutions of much higher concentrations. Maximum gelatinisation temperatures or melting points approach the limiting value, 33°–35°, as the concentration of gelatin increases. At these maximum temperatures, gelatinisation is produced by the presence of a certain definite minimum proportion of form *B* required for the formation of a jelly; above 35°, gelatinisation does not take place at any concentration.

The existence of two forms of gelatin, on which gelatinisation of the solutions is dependent, is confirmed by the behaviour of such solutions with alcohol, which at temperatures below 30° either precipitates the gelatin or renders the solutions opalescent if present to the extent of 15%; if the concentration of the gelatin is high, alcohol precipitates an opalescent jelly. Above 35°, the precipitation requires far larger proportions of alcohol (45–50%), unless a comparatively large amount of an electrolyte is also added. Further confirmation is afforded by the results of measurements of osmotic pressure (compare Moore and Roaf, *A.*, 1907, ii, 73), viscosity (von Schroeder, *A.*, 1903, ii, 721), and “gold numbers” (Menz, *A.*, 1909, i, 343).

Gelatin sols dried at above 35° and gels dried at below 15° give different solid forms, and whilst the solid gelatin thus obtained may or may not be in the form in which it exists in the material from which it is prepared, there is some indication that the solid gelatin prepared by drying sols above 35° is the form existing in the sols.

T. H. P.

Pepsin. I. Chemical Changes in the Purification of Pepsin. LEWIS DAVIS and HARVEY M. MERKER (*J. Amer. Chem. Soc.*, 1919, **41**, 221–228).—The purification of commercial pepsin by fractional precipitation, salting-out, filtration, and dialysis is accompanied by gradual elimination of the secondary protein derivatives, including amino-acids, the purified samples tending more and more to approach the proteins in character as the proteolytic activity increases; the proportion of material coagulable by heat also increases. The fact that the most active samples respond strongly to Molisch's test indicates the possibility that the pure enzyme may be a conjugated protein, probably a gluco-protein. The proportion of mineral matter present also diminishes continuously as purification proceeds; the sulphur and calcium appear, however, to be unaffected, although the phosphorus content shows a marked decrease and chlorides are apparently eliminated entirely. Other than the increase resulting from removal of non-nitrogenous impurities, there is little apparent change in the proportion of total nitrogen.

The diminution in the α -amino-acid content is almost proportional to the increase in proteolytic activity, and the small amount of α -amino-acid in the most active sample, which exhibits an almost neutral reaction, appears to correspond with lysine. It seems probable that the concentration of hydrogen ions in solutions of the

pure enzyme, could this be obtained, would be comparable with the low values given by other proteins.

The optical activities of the enzymes of different degrees of purity were measured, but the same values were obtained with pepsins showing different proteolytic activities. The rennetic activities correspond closely with the proteolytic activities.

T. H. P.

A Delicate Method of Determining Invert Activity. C. K. WATANABE and V. C. MYERS (*Proc. Soc. Exp. Biol. Med.*, 1918, **15**, 142—143; from *Physiol. Abstr.*, 1919, **3**, 502).—The method is similar to that advocated by Myers and Killian (compare A., 1917, i, 369) for measuring diastatic activity, but in this case sucrose solution is substituted for the solution of soluble starch or glycogen.

W. G.

Influence of Hydrogen-ion Concentration on the Enzymic Activity of Three Typical Amylases. H. C. SHERMAN, A. W. THOMAS, and M. E. BALDWIN (*J. Amer. Chem. Soc.*, 1919, **41**, 231—235).—The enzymes examined were the amylases of pancreas, malt, and *Aspergillus oryzae*, representing the starch-splitting enzymes of the higher animals, higher plants, and fungi respectively. Experiments were made to determine as definitely as possible the hydrogen-ion concentrations which induce optimal activity of the pancreatic and fungus amylases, and to establish for each of the three amylases the limits of hydrogen-ion concentration within which any enzymic activity is shown and the form of the curve representing the activities at all concentrations of the hydrogen ion between these limits. The experimental methods used were those previously described (A., 1915, i, 183), except that greater precautions were taken to prevent any action of light during the enzymic actions, and that, in measuring the hydrogen-ion concentration by the electrometric method, the current of hydrogen was replaced by a Clark cell and a rocking electrode.

The results of Sherman and Thomas (*loc. cit.*) on the optimum hydrogen-ion concentration for malt amylase were confirmed and that for pancreatic amylase more sharply defined; that for the maltase of *Aspergillus oryzae* is closer to the value for malt amylase than to that for the pancreatic enzyme. The latter is active for values of P_H 4—10, the optimal activity being at about 7; the solutions commonly considered neutral show under similar conditions the value 5·8 for P_H . Malt amylase is active for P_H 2·5—9, the optimal activity being at 4·4—4·5, whilst with the *Aspergillus* enzyme the limits of P_H are 2·6 and 8 and the optimum 4·8. The influence of the concentration of the electrolyte, as distinguished from the concentration of the hydrogen ion alone, appears to be greatest with pancreatic amylase and least with the amylase of *Aspergillus oryzae*.

T. H. P.

Effect of Neutral Salts on the Activity of Ptyalin. ELBERT W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1919, **41**, 228—230).—The

methods used in this investigation were essentially those previously described (A., 1917, i, 358; 1918, i, 274). Ammonium chloride and nitrate, and, to a less extent, the sulphate and thiocyanate, enhance the hydrolytic action of ptyalin on starch. The effects of the ammonium salts of organic acids are much smaller; the acetate, but not the oxalate, shows some power as an auxo-amylase, whilst the tartrate exerts a slight stimulating action. Ammonium chloride and bromide produce marked increase in the amount of starch hydrolysed, the quantity of reducing products being the same in each case; the fluoride inhibits the action. Similar results are obtained with the sodium haloids. The effect of sodium chloride is not altered by changing the cation to potassium or calcium, so that the action of a salt is a function, not of the cation, but of the anion. The trivalent cations were not tested, owing to the coagulating effect of their soluble salts on colloids.

Tests made by means of Nessler solution at intervals during the action of ptyalin on starch in presence of an ammonium salt show that the ammonium ion is not destroyed during the digestion.

T. H. P.

Photochemical Effect of certain Fluorescent Substances on Rennin. JANET H. CLARK (*Amer. J. Physiol.*, 1918, **47**, 251—264; from *Physiol. Abstr.*, 1919, **3**, 502).—The inhibition of rennin by light is attributed to the formation of toxic substances as a result of photochemical action. This may be accompanied by fluorescence, and fluorescence may or may not be accompanied by the formation of toxic substances. Free halogens are the toxic substances in the experiments described with eosin and erythrosin.

W. G.

Simple Method of Making *p*-Arsanilic Acid. PHILIP ADOLPH KOBER and WALTER S. DAVIS (*Proc. Soc. exp. Biol. Med.*, New York, 1918, **16**, 13—15).—1000 c.c. of crude 75% arsenic acid are concentrated to about 100 c.c. by heating for twelve to fifteen hours in an open beaker in an oil-bath at 120—140°. After cooling, the acid is slowly added, with vigorous stirring, to 1400 c.c. of dry aniline, at or below 0°. The mixture becomes viscous, then granular, and is finely ground. 200 Grams of it are heated in a flask and stirred until the powder melts; it is then heated for one and a-half hours at 160—170° and one hour at 180—183°, under a reflux condenser. After cooling, 450 c.c. of 3*N*-hydrochloric acid are added, the aniline is separated off, the solution is shaken with 15—20 grams of kaolin or infusorial earth, and filtered with aid of suction. To the clear filtrate, 100 c.c. of 6*N*-hydrochloric acid are added, and then, on an aliquot portion, the further amount of hydrochloric acid is determined by trial, which will give the maximum crystallisation on keeping. This, added to the main bulk, yields 30% of crystalline primary arsanilic acid, without any secondary acid. The usual mistake in the laboratory is to employ too much aniline and too high a temperature.

G. B.

Method of Preparing Pure Dihydrochloride of Diamino-dihydroxyarsenobenzene [Salvarsan]. PHILIP ADOLPH KOBER (*Proc. Soc. exp. Biol. Med., New York*, 1918, **16**, 23—24).—The author dislikes the precipitation of the dihydrochloride from methyl alcohol by ether, and prefers the mass action of strong hydrochloric acid in aqueous solution. The alkaline solution of the base is slightly acidified with hydrochloric acid, and the solution is poured slowly, with vigorous stirring, at a low temperature into hydrochloric acid (1 in 1, or more dilute). This obviates coagulation of the flocculated particles. G. B.

Halogenation. XVII. Action of Halogens on the Grignard Reagent and Replacement of Halogen Atoms by one another. BASIK LAL DATTA and HARAPARBUTTY KUMAR MITTER (*J. Amer. Chem. Soc.*, 1919, **41**, 287—292).—Few investigations have been made on the action of halogens on the Grignard reagent. The authors find that one halogen is, in general, able to displace other halogens from the Grignard reagent with the production of the corresponding haloid derivatives, the yield of the latter being greatly influenced by the nature of the halogen and by the experimental conditions; the reaction is sometimes accompanied by secondary reactions due to the union of the Grignard residues.

When iodine is added to magnesium phenyl bromide, the resultant products are iodobenzene in 25—30% yield, benzene in 30—40% yield, and a small proportion of diphenyl, but addition of magnesium phenyl bromide to ethereal iodine solution gives phenyl iodide in 90% yield. By the action of iodine on magnesium phenyl iodide, iodobenzene, benzene, and diphenyl are formed, the last constituting the main product. The action of iodine on magnesium *o*-tolyl bromide gives *o*-iodotoluene in 80% yield. From *m*-bromotoluene, *m*-iodotoluene is similarly obtained in 76% yield, as well as a little unchanged *m*-bromotoluene; from *p*-bromotoluene, in addition to a little unchanged substance, *p*-iodotoluene is formed in 74% yield. By the action of iodine on magnesium ethyl iodide, ethyl iodide in low yield is obtained.

Similarly, in the action of bromine on magnesium phenyl iodide, benzene and bromobenzene are the principal products, the yield of the latter being 30—40%; a small proportion of diphenyl is also obtained. From magnesium phenyl bromide, bromobenzene is obtained in 30—40% yield. By the action of bromine on magnesium ethyl iodide, ethyl bromide is formed, and from magnesium *n*-propyl iodide, propyl bromide is formed in 30—40% yield.

The action of chlorine on magnesium phenyl bromide gives a product which explodes with great violence when shaken. From *p*-bromotoluene, *p*-chlorotoluene is obtained in 20% yield.

T. H. P.

Physiological Chemistry.

The Coagulation of Blood. MARIO CHIO (*Arch. Farm. speriment.*, 1918, **25**, 175—192, 193—212; from *Chem. Zentr.*, 1918, ii, 1048).—The behaviour towards hydrochloric acid and carbon dioxide (A., 1917, i, 672) varies with the season of the year in such a manner that, during the warmer months, smaller concentrations of hydrochloric acid are sufficient to prevent the coagulation of the salt plasma, whilst, on the other hand, higher tensions of carbon dioxide are necessary. It is advisable, although not absolutely necessary, to perform the experiments at constant temperature. New experiments have shown that a displacement of the chemical equilibrium in dilute salt plasma occurs, which is shown by an increase in alkalinity. Hydrolysis of fatty matter must, among other influences, be a cause and consequence. Hydrolytic fission of alkali soaps liberates fatty acids, which yield calcium soaps in the presence of soluble and dissociable calcium salts. Changes therefore occur in the condition of certain colloids, which result first in the formation of gels and subsequently in contraction, owing to diminution in the irrigation of the lipoid-albumin complexes. Increase in the tension of carbon dioxide diminishes the rate of this phenomenon. The coagulation of blood may be explained by the formation of calcium soaps by a process which can be limited or prevented by suitable adjustment of the carbon dioxide tension both outside and within the organism. II. W.

Proteolytic Relationships in the Serum of the Horse and Ox. S. G. HEDIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 11—47).—A continuation of the work of Hedin and Masai (A., 1918, i, 90). The chief results may be summarised as follows: The serum shows itself either completely inactive or very slightly active towards casein, but undoubtedly capable of breaking down peptone when tested by the tannic acid method. If the serum is fractionated with ammonium sulphate, the globulin fraction, precipitated by about one-third saturation, contains primary and secondary proteases, and thus causes fission of casein and peptone. The first type of activity appears to be lost if the serum is heated at 56° during thirty minutes, whereas the second type persists in a greatly lessened degree. The albumin fraction precipitated between half and full saturation contains practically only secondary proteases, which are active towards peptone but not noticeably towards casein; it contains also substances which inhibit the activity of pancreas trypsin as well as of the primary proteases of the globulin fraction. The power of these inhibiting substances is destroyed or weakened by treating the albumin with chloroform or ether; if, however, they have already acted on the enzyme, subsequent treatment with chloroform is ineffective. H. W.

The Increase in Nitrogen Metabolism of the Dog, following the Administration of Desiccated Thyroid Gland. ALICE RONDE and MABEL STOCKHOLM (*J. Biol. Chem.*, 1919, **37**, 305—316).—Nitrogen elimination in the dog receiving only sugar solutions may be increased approximately 50% by the administration, during a five- to seven-day period, of commercial desiccated thyroid gland in doses of 0.10—0.15 gram per kilo. of body weight. W. G.

The Acid-Base Balance in Animal Nutrition. I. The Effect of certain Organic and Mineral Acids on the Growth, Well-being, and Reproduction of Swine. ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 317—328).—With the view of testing the ability of swine to metabolise successfully the lactic and acetic acids of silage, four lots of two pigs each, all from the same litter, were fed with equal amounts of a good basal ration consisting of ground corn 80%, meat meal tankage 15%, standard wheat middlings 5%. One lot served as a control and the other three received in addition, respectively, sulphuric, lactic, and acetic acids in amounts increasing gradually up to 500 c.c. of *N*-acid per pig per day during 150 days. The three acid-fed lots grew practically as rapidly as the control, and remained in equally good condition. The organic acids seemed to be completely oxidised, and the sulphuric acid was neutralised without apparent harm or significant effect on growth. An examination of the blood at the end of the experiment showed that neither the organic nor mineral acids disturbed the reaction of the blood.

The two pigs fed with sulphuric acid were continued on the same ration for four to six months longer, and successfully produced young, but either the excessive amount of acid fed or some other factor prevented the successful rearing of the young. W. G.

The Acid-Base Balance in Animal Nutrition. II. Metabolism Studies on the Effect of certain Organic and Mineral Acids on Swine. ALVIN R. LAMB and JOHN M. EVVARD (*J. Biol. Chem.*, 1919, **37**, 329—342. Compare preceding abstract).—Metabolism studies on a growing pig fed on a ration containing a liberal allowance of calcium show that the animal apparently oxidised the organic acids (lactic and acetic) completely with no increase in urinary ammonia, and that the acids seemed to bring about a slightly increased retention of calcium. On the same basal ration plus 300 c.c. of *N*-sulphuric acid per day, 61% of the acid ingested was neutralised by means of ammonia, and 4.6% was accounted for by extra urinary acidity. On another basal ration very low in calcium, extra ammonia excretion accounted for 76% of the acid fed, and extra urinary acidity for 10%. On neither ration did the mineral acid cause a significant loss of calcium, nor did it interfere with the storage of protein. W. G.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins. F. MAIGNON (*Compt. rend.*, 1919, **168**, 474—476. Compare A., 1918, i, 416).—The author con-

siders that the fats exercise a favourable action on the assimilation of albumin by intervening in the synthetic reconstitution of the proteins, and that in this action not only the glycerol portion of the fat molecule exercises an influence as already shown by Mailard, but also the fatty acid portion. Thus the fatty acids may combine with the amino-acid nucleus of a protein in formation and permit of the building up of a molecule, which it would not have been possible to obtain simply with the amino-acids available and without the assistance of the fats. W. G.

A Method of Expressing Numerically the Growth-promoting Value of Proteins. THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, **37**, 223—229).

From feeding experiments with rats in which the proportion of protein in the food was so restricted that the protein factor alone determined the rate of growth, the authors determined, within limits, the concentration which promoted the greatest gain of body weight relative to the protein ingested by supplying foods containing different percentages of protein. The results indicate, in the first place, the necessity for employing a large number of animals. When an animal is restricted to such a quantity of protein that a maximum gain of body weight is made per unit of protein eaten, it grows at less than the normal rate. Economy in nutrition during growth depends on a correct adjustment between the proportion of protein and the total energy supplied, the optimum of protein being determined not only by the absolute amount furnished, but also by its quality. W. G.

Accessory Factors in the Nutrition of the Rat. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 408—415).—An antiscorbutic does not fulfil the physiological function of the fat-soluble *A* when it replaces it in the diet of the rat. The authors confirm the observation of McCollum and co-workers and of Drummond that by depriving rats of the antineuritic factor a dietetic deficiency is brought about, as a result of which a fatal termination ensues if the diet is not rectified in time. Rats subsisting on a diet containing the antiscorbutic factor as well as the water-soluble and fat-soluble *A* factors grow better than rats from the diet of which the antiscorbutic factor is absent. W. G.

Antiscorbutic Properties of Concentrated Fruit Juices. ARTHUR HARDEN and ROBERT ROBISON (*J. Army Med. Corps*, 1919, **32**, 48—56).—Orange-juice, evaporated at 40° under reduced pressure, gives a solid residue in which the antiscorbutic principle is still largely intact and remains so in a dry atmosphere at the ordinary temperature for six months. Apple jelly prepared in a Kestner evaporator also possesses antiscorbutic properties in a high degree, but is inferior to orange juice. G. B.

Dietary Properties of the Pea (*Vicia sativa*). E. V. MCCOLLUM, N. SIMMONDS, and H. T. PARSONS (*J. Biol. Chem.*, 1919, **37**, 287—301).—Pea proteins are of very poor quality when

fed as the sole source of nitrogen. Casein and zein supplement the deficiencies of the pea proteins, but gelatin and lactalbumin do not. There is an indication of the presence in peas of some substance or substances which prove injurious when taken in large amounts, but the toxicity, if there be any, is but slight and only manifests itself when diets extremely rich in peas are persisted in over a long period.

From the failure of lactalbumin to supplement the proteins of the pea, or to induce growth when fed in the amounts used in the experiments described, the authors tentatively conclude that lactalbumin is either an incomplete protein or a poorly constituted one.

W. G.

Zinc, a Cellular Constituent of the Animal Organism. Its Presence and Rôle in the Venom of Serpents. C. DELEZENNE (*Ann. Inst. Pasteur*, 1919, **33**, 68—136).—Of the zinc occurring in the blood of animals, the major portion is found in the leucocytes, a little in the red corpuscles, and practically none in the plasma. An examination of the different organs of a number of animals of different species shows that zinc is a constant constituent of all animal cells. In the venom of serpents it is present to the extent of 0.31—0.56% in the venom of Colubrids and 0.11—0.23% in that of Viperids, and is present, combined with organic constituents, in such a manner as not to be precipitated by hydrogen sulphide or separated by dialysis even in the presence of hydrochloric acid. It is probably combined with a proteose rich in sulphur, since the sulphur and zinc contents of the different venoms examined varied very closely in the same direction. The proportion of zinc present in the venoms was found to vary inversely with the proteolytic and coagulating properties of the venoms. On the other hand, the zinc content was found to run parallel with the nucleolytic activity and the diastatic activity, which gives rise to hæmolysis, venoms with high zinc content showing the greatest activity in these two directions. In this connexion it should be noted that in mammals it was found that those organs which were richest in phosphatides and nucleic acids had the highest zinc contents.

W. G.

Behaviour of the Kidneys towards some Isomeric Sugars (Dextrose, Lævulose, Galactose, Mannose, and Sucrose, Maltose, Lactose). H. J. HAMBURGER and R. BRINKMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 548—561).—When Ringer's solution containing dextrose is passed through the kidneys (of frogs), this sugar is retained by the glomerulus membrane, whereas lævulose and mannose are allowed to pass entirely and galactose to a large extent. Sucrose, maltose, and lactose also pass through this membrane, the last perfectly; the membrane is also permeable to raffinose.

T. H. P.

The Physicochemical State of the Proteins in Cow's Milk.

LEROY S. PALMER and ROBERT G. SCOTT (*J. Biol. Chem.*, 1919, **37**, 271--284).—Samples of fresh skim-milk, skim-milk preserved either with 5% of chloroform or 0.05% of formaldehyde, and of the lactic acid whey from fresh skim-milk were filtered, under pressure, through Pasteur-Chamberland tubes, and in the filtrate the total protein, as precipitated by Almen's tannic acid reagent, and the non-protein nitrogen were determined. The amount of non-casein protein recovered in the filtrate did not in any case exceed 10% of the non-casein protein in the original milk, and in most cases was considerably less than this figure. There was also only a partial recovery of the non-protein nitrogen of the original milk in the experiments with milk preserved with chloroform and formaldehyde. These results differ widely from those of Van Slyke and Bosworth (compare A., 1915, i, 192). The authors consider that it is fallacious to draw conclusions regarding the true state of solution of non-casein proteins of milk based on filtration studies of this character, since there is considerable variation in size of the pores of different Pasteur-Chamberland filters. W. G.

The State of Proteins in Cow's Milk.

L. L. VAN SLYKE and A. W. BOSWORTH (*J. Biol. Chem.*, 1919, **37**, 285--286. Compare A., 1915, i, 192).—A reply to Palmer and Scott (compare preceding abstract). W. G.

Creatinuria and Acidosis.

W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **37**, 245--252).—Feeding experiments carried out with two normal boys, four women suffering from hyperthyroidism, and two normal women did not demonstrate any definite connexion between changes in acid-base equilibrium and creatine excretion. W. G.

Chemistry of Vegetable Physiology and Agriculture.**The Effect of Acids on the Growth of *Bacillus coli*.**

FRANK JOHN SADLER WYETH (*Biochem. J.*, 1918, **12**, 382--401).—All strains of *Bacillus coli*, whether of human or bovine origin, behave similarly when exposed to similar conditions. The degree of acidity of the final reaction produced by a culture of *B. coli* cannot be used for diagnostic purposes, the value not being a "physiological constant," but dependent on (a) the initial hydrogen-ion concentration of the medium in which fermentation occurs; (b) the composition of the medium, especially the degree to which it is "buffered"; (c) the nature of the acid used to produce the initial reaction of the medium. When the amount of acid added is insufficient completely to inhibit the fermentation

of *B. coli* therein, a definite latency of growth results, the latency increasing with the amount of acid initially added. Each acid has its own specific effect in inhibiting the growth of *B. coli* in a given medium, the inhibiting effect being greater as the acid is more highly dissociated. For a mixture of any given medium and acid, there appears to be a definite critical point, beyond which the slightest rise in the degree of acidity results in a complete inhibition of the growth of *B. coli*.
W. G.

Effect of Carbon Disulphide and Toluene on Nitrogen Fixing and Nitrifying Organisms. P. L. GAINEY (*J. Agric. Res.*, 1918, 15, 601—614).—Carbon disulphide and toluene, if applied to soils in sufficient quantity, will destroy *Azotobacter* and check the accumulation of nitrates, and possibly will destroy nitrifying organisms. The amounts of these two antiseptics necessary to produce this effect vary widely with the conditions, being affected particularly by the moisture content of the soil, diminishing as the latter increases. Providing that sufficient antiseptic is added to have any effect on *Azotobacter*, they are usually completely destroyed, but, on the other hand, there is a great difference in the amount necessary to destroy nitrifying organisms and that necessary to check their activity. Unless nitrification has been checked, there is no appreciable accumulation of ammonia following the treatment with these antiseptics.

There are nitrogen-fixing organisms other than *Azotobacter* present in soils, which are not destroyed by the addition of 10 c.c. of carbon disulphide or toluene to 100 grams of soil, even when the moisture content of the soil is high.
W. G.

Production of Citric Acid by *Sterigmatocystis nigræ* [*Aspergillus niger*]. MARIN MOLLIARD (*Compt. rend.*, 1919, 168, 360—363).—In culture solutions containing insufficient quantities of nitrogen and mineral salts for the sugar present, *Aspergillus niger* produces citric rather than oxalic acid, the amount increasing gradually at first, and then considerably between the eighth and tenth days, after which it remains almost constant. Citric acid is noticeable from the very first, but oxalic acid only appears towards the end of the second day, just at the time when the conidiæ commence to be formed, its amount only increasing very slowly.
W. G.

Course of the Formation of Diastase by *Aspergillus niger*. F. A. F. C. WENT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 479—493).—*Aspergillus niger* was grown in the dark at $24 \pm 0.5^\circ$ in a culture solution containing 5% of dextrose, 0.5% of ammonium nitrate, 0.1% of potassium phosphate, and 0.05% of magnesium sulphate in glass flasks, the amount of diastase present in the liquid and in the fungus mass being determined at first daily and later every two, three, or more days. The method of determination consisted in ascertaining the length of time necessary

for the complete disappearance of the starch from a starch solution of definite strength mixed with the enzyme solution. The tests were made with a solution containing 0.0625 gram of iodine and 0.0625 gram of potassium iodide to 100 grams of water, 1 c.c. of this being found to give a distinct blue coloration with 0.001 gram of soluble starch, or a definite reddish-violet coloration with 0.0002 gram, in 10 c.c. of water.

During the first days after germination of the mould spores with which the culture liquid was inoculated, a great quantity of diastase is formed in the mycelium, this being accompanied by destruction of the enzyme, which is at first negligible in comparison with the formation, but soon makes itself so evident that the total quantity of diastase quickly decreases from the maximum reached about five days after the commencement of germination. Never more than a very small part of the total amount of the enzyme occurring in the mycelium passes into the nutrient solution, this being perhaps derived partly from dead cells.

T. H. P.

Occurrence of Iodine in Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1918, **104**, 54—58).—The author has examined a considerable number of plants in respect of iodine content. The method employed consisted in ashing the plant in an alkaline condition and treatment of the residual mixture of salts with 95% alcohol, in which any iodides are soluble. The aqueous solution of the extract was treated with a solution of nitrosylsulphuric acid in concentrated sulphuric acid in the presence of chloroform, in which any liberated iodine dissolved to a red solution. Test experiments showed that 0.04 mg. of added iodine could be detected in 10 grams of spinach by this method.

Minute amounts of iodine are shown to occur in *Beta vulgaris*, *Solanum tuberosum*, *Apium graveolens*, *Lactuca sativa*, and *Daucus carota*. Iodine could not be detected in the fruit, seeds, tubers, or leaves of *Tarax baccata*, *Pinus silvestris*, *P. cembra*, *Abies pectinata*, *Zea Mays*, *Oryza sativa*, *Avena sativa*, *Hordeum sativum*, *Secale cereale*, *Triticum sativum*, *Allium cepa*, *Fagus sylvatica*, *Castanea vesca*, *Cannabis sativa*, *Urtica dioica*, *Polygonum jagopgrum*, *Spinacea oleracea*, *Lepidium sativum*, *Ribes grossularia*, *Pirus malus*, *P. communis*, *Prunus cerasus*, *Lupinus albus*, *L. angustifolius*, *Trifolium pratense*, *Vicia sativa*, *Pisum sativum*, *Soja hispida*, *Phaseolus vulgaris*, *Vitis vinifera*, *Stachys tubrifera*, *Curcubita pepo*, or *Aesculus hippocastanum*, or in the following fungi: *Cantharellus cibarius*, *Boletus edulis*, *Agaricus campestris*.

Iodine could not be detected in eight samples of milk, in five varieties of cheese, or in cow's urine.

H. W.

Chemical Composition of *Agave americana*, L. The Chemistry of Succulent Plants in General. JULIUS ZELLNER (*Zeitsch. physiol. Chem.*, 1918, **104**, 2—10).—The leaves of *Agave americana*, L., have been submitted to chemical examination along

the usual lines. The fresh leaves are remarkable for their high water content. For examination, the air-dried material was taken. The light petroleum extract (1·03%) contained fat, chlorophyll, and wax; the ethereal extract (0·74%) consisted of waxy matter. The aqueous extract (50·75%) was composed of amorphous carbohydrates (12·00%), sugar (calculated as dextrose, 12·68%), malic acid (about 8%), free acid (as H ions, 0·02%), ash (7·54%), other matter, such as small amounts of peptones, amino-acids, etc. (about 10%). The portion insoluble in indifferent solvents contained crude cellulose, including bast fibres (17·85%), pentosans (7·44%), methylpentosans (1·01%), pectin, hemicelluloses, oxalate (about 13%), mineral matter (4·82%), crude protein (3·25%).

The results are compared with those obtained from the examination of other succulent plants so far as the data are available. The high content of water-soluble substance, of calcium malate, of pectinous matter, and probably of sugar appears to be characteristic of the class, but it is not possible at present to decide whether the poverty in nitrogen and iron is a general feature. Further, it would appear that a volatile substance, probably an aldehyde, is frequently present in this class of plant.

H. W.

Is Selenium Present in the Vegetable and Animal Organism? R. FRITSCH (*Zeitsch. physiol. Chem.*, 1918, 104, 59—64).—According to Gassmann (A., 1916, i, 772; 1917, ii, 540), selenium is to be regarded as a definite constituent of the human, vegetable, and animal organisms. The author, however, considers that the methods on which Gassmann relies cannot give trustworthy results. He has therefore examined the question further, and has been unable to detect the presence of selenium in thirty-five samples of spinach, clover, corn, potatoes, or bones. The method adopted consisted of ashing the plant in the presence of sodium carbonate and sodium nitrate, and finally obtaining any selenium present as a solution of selenious acid in concentrated sulphuric acid; in this solution, the presence of selenium is detected by the green to bluish-green coloration with codeine, or the intense yellow coloration with colchicine. Test experiments showed that 2—0·5 mg. of selenious acid could be detected in 30—50 grams of plant material in this manner.

Selenium does not appear to be present in urine or bones.

H. W.

The Microchemical Detection and the Distribution of Soluble Oxalates in the Vegetable Kingdom. H. MOLISCH (*Flora*, 1918, 11—12, 60—70; from *Physiol. Abstr.*, 1919, 3, 540).—The methods employed by the author to ascertain the presence of soluble oxalates in plants were precipitation with (1) saturated alcoholic sodium hydroxide; (2) saturated alcoholic potassium hydroxide; (3) lead acetate; (4) barium chloride. Two hundred and forty plant species were examined. Soluble oxalates were found frequently in the phanerogams, and the following families

contained large quantities: Polygonaceæ, Chenopodiaceæ, Amarantaceæ, Aizoaceæ, Begoniaceæ, Milostomaceæ, Oxalideæ, Cannaceæ, and Marantaceæ. W. G.

Spectrographic Study of the Ashes of Marine Plants.

EUGÈNE CORNEC (*Compt. rend.*, 1919, 168, 513--514).—From a spectrographic study of the ashes of *Laminaria*, the presence of the following elements was shown: Group I, silver, arsenic, cobalt, copper, manganese, nickel, lead, and zinc; Group II, bismuth, tin, gallium, molybdenum, and gold; Group III, antimony, germanium, glucinum, titanium, tungsten, and vanadium. The elements of Group I have previously been detected in marine plants, those of Group II in sea-water, whilst those of Group III have not been previously reported as occurring either in sea-water or in marine plants. Gold, bismuth, germanium, and gallium were only present in spectrographic traces in the ashes examined. W. G.

Application of the Biochemical Method to the Study of the Leaves of *Hakea laurina*. Extraction of a Glucoside (Arbutin) and of Quebrachitol. EM. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1919, 168, 414--417).

—From a study of the rotation of an extract of the leaves of *Hakea laurina*, R. Br., made by alcohol, after subsequent defecation and removal of the alcohol, first directly and then after the action, first, of invertase, and, secondly, of emulsin, the authors show the presence of sucrose, of two glucosides, and of a levorotatory substance, not hydrolysable by emulsin, in the leaves. By the use of suitable solvents they have isolated quebrachitol and arbutin in their crystalline forms and characterised them. W. G.

Ovalbumin Constitutes a Complete Food for *Isaria densa*.

MARIN MOLLIARD (*Compt. rend.*, 1919, 168, 523--524).—Ovalbumin, prepared from the commercial material by solution in water and subsequent coagulation by heat in such a manner as to obtain it as a very finely flocculated mass which is filtered off and strongly pressed, satisfies all the nutritive requirements of *Isaria densa*. The phenomena of intense oxidation of ovalbumin give rise to a very low respiratory quotient and the formation of oxalic acid. W. G.

The Microchemical Reactions and Localisation of the Alkaloid of *Isopyrum thalictroides*, L. MARCEL MIRANDE (*Compt. rend.*, 1919, 168, 316--317).

—The author gives a number of microchemical tests for detecting the presence of the alkaloid, isopyrine, in the plant cells, and shows that it occurs, in the case of *Isopyrum thalictroides*, principally in the subterranean organs, which are at all seasons very rich in the alkaloid and to a less extent in the green aerial organs. [See, further, *J. Soc. Chem. Ind.*, 1919, 197A.] W. G.

Organic Chemistry.

Graphic System of Representing Hydrocarbons. WA. OSTWALD (*Chem. Zeit.*, 1919, **43**, 121—122).—If the percentage and relative proportional composition of hydrocarbons be graphically represented in a system in which the ratios of the percentages of hydrogen and carbon form the ordinates and the ratios of the number of atoms of hydrogen to carbon form the abscissæ, the connected points of intersection form a straight line terminated at one end by methane and at the other by pure carbon. On this line there are two well-marked points, that occupied by the olefines with the ratio of $H:C=2:1$ and the ratio of the percentages of $H:C=0.167$, and that occupied by benzene and acetylene with $H:C=1:1$ and $\%H:\%C=0.083$. The first point is approached by the paraffins, starting from methane, whilst the second point forms the starting place for the series of aromatic and acetylene hydrocarbons with increasing molecular weight (in the upward direction towards the olefine point), and also for the hydrocarbons rich in carbon and with many rings in their structure (in the downward direction leading towards pure carbon). By dropping as perpendiculars on to the line the molecular weights, a co-ordinated system is obtained in which, in the case of homologous series, the atoms of carbon as lines cut the atoms of hydrogen as curves. Analogous representations are obtained when the percentage of hydrogen and atoms of hydrogen, the percentage of carbon and atoms of carbon, the percentage of hydrogen and atoms of carbon, and the percentage of carbon and atoms of hydrogen are chosen as co-ordinates. For example, in a graphic representation on the last-named system, benzene, naphthalene, and anthracene lie on one curve, the continuation of which leads to chrysene, picene, and other hydrocarbons of multi-ringed structure. In the whole field, homologous series fall together in lines which show recognised chemical relationships.

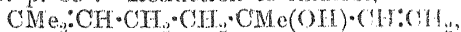
C. A. M.

Production of Ethyl Alcohol from Algæ. ED. KAYSER (*Ann. Chim. anal.*, 1919, [ii], **1**, 79—80).—The marine algæ *Laminaria flexicaulis* and *L. saccharina*, when heated with water under pressure, yield a liquid which ferments readily; about 3.7 litres of alcohol are obtained per 100 kilos. of dry algæ. If the digestion is made with 7% sulphuric acid and the liquid obtained nearly neutralised before fermentation, the yield of alcohol may be increased to about 12 litres. [See, further, *J. Soc. Chem. Ind.*, 1919, 266A.]

W. P. S.

Synthesis of Linalool. L. RUZICKA and V. FERNASIR (*Helv. Chim. Acta*, 1919, **2**, 182—188).—Tiemann and Semmler's formula for linalool has now been confirmed by synthesis. Methylhepten-

one (from citral; Verley, A., 1898, i, 557) is dissolved in ether, mixed with finely powdered sodamide, and then submitted to a slow current of acetylene at a low temperature, when a good yield of *dehydrolinalool*, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}(\text{OH})\cdot\text{CH}\cdot\text{CH}_3$, is obtained. This is a colourless, mobile oil, b. p. $91-93^\circ/12$ mm., D^{15}_D 0.8855, with an odour like citral, and it forms a *phenyl-carbamate*, m. p. 88° . Reduction to linalool,



is effected by shaking an ethereal solution of the oil with thin shavings of sodium (8 atomic proportions) applied in four separate portions, a few drops of water being added from time to time.

J. C. W.

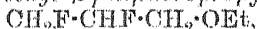
Spontaneous Inflammation of Mixtures of Air and Ethyl Ether Vapour. E. ALILAIRE (*Compt. rend.*, 1919, 168, 729-730).

—Under the experimental conditions, it was found that spontaneous inflammation of a mixture of air and ethyl ether vapour occurred at about 190° , when the amount of ether in the gaseous mixture was 1 gram per litre. No reaction took place at the ordinary temperature.

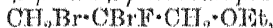
W. G.

Ethyl Fluorobromopropyl Ether and Ethyl Fluoroallyl Ether. FRÉD. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 103-107).

—Ethyl allyl ether when brominated yields *ethyl dibromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. $103.5^\circ/35$ mm., which when heated with mercurous fluoride or silver fluoride gives ethyl bromide and a certain amount of *ethyl β -fluoro- γ -bromopropyl ether*, $\text{CH}_2\text{Br}\cdot\text{CHF}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. $156.4-157.3^\circ$, D^{16}_D 1.41^{ms} together with a little *ethyl $\beta\gamma$ -difluoropropyl ether*



b. p. 114.5° . When heated with sodium methoxide in meth^a-alcoholic solution, ethyl fluorobromopropyl ether yields *ethyl β -fluoroallyl ether*, $\text{CH}_2\text{CF}\cdot\text{CH}_2\cdot\text{OEt}$, b. p. 77.5° , $D^{15.1}_D$ 0.9165^{er} n_D 1.37665, n_D 1.3790, n_D 1.38874, which readily combines with bromine, giving *ethyl β -fluoro- $\beta\gamma$ -dibromopropyl ether*,



b. p. 188° .

W. G.

Action of Alkyl Iodides on Normal Sodium Phosphate in Aqueous Solution. OCTAVE BAILLY (*Compt. rend.*, 1919, 168, 560-563).

—The lower members of the series of alkyl iodides react with normal sodium phosphate in aqueous solution when heated in sealed tubes at 60° or 100° , giving the disodium alkyl phosphates and a small amount of the monosodium dialkyl phosphates. The yield diminishes rapidly from 73.5% in the case of methyl iodide to 10.6% in the case of isobutyl iodide as the molecular weight increases. The following normal alkali and alkali-earth salts of the alkyl phosphates have been prepared: *strontium, potassium, ammonium, and sodium methyl phosphates; strontium and sodium ethyl phosphates; calcium and strontium propyl phosphates;*

calcium, strontium, and sodium isopropyl phosphates; calcium and strontium isobutyl phosphates; strontium allyl phosphate. The solubility of the alkali-earth alkyl phosphates diminishes from the barium salts through the strontium salts to the calcium salts, which are almost insoluble.

W. G.

Formic Acid is as much an Aldehyde. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1918, **16**, 438—441).—From a study of the heats of formation and combustion of formic acid, the author concludes that, under the conditions of temperature and pressure prevailing when combustion occurs, formic acid behaves as a mixture of equal parts of the tautomeric acid and hydroxy-aldehyde forms.

W. G.

Nature of the Fatty Acids produced by the Oxidation of Brown Coal Tar Oil. C. HARRIES (*Ber.*, 1919, **52**, [B], 65—72).—The fatty acids produced by treating brown coal-tar oil (freed from solid paraffins and phenols, and then having b. p. 125—220°/10 mm.) with ozone and decomposing the resulting ozonides (Harries, Koetschau, and Fonrobert, *Chem. Zeit.*, 1917, **16**, 117) have been esterified by Fischer's method, and the esters separated by fractional distillation. Formic, acetic, propionic, oxalic, palmitic, stearic, and myristic acids have been identified, and two other acids, probably heptic and octic acids, isolated. The complete absence of the fatty acids $C_4H_8O_2$ — $C_6H_{12}O_2$ is remarkable.

C. S.

Preparation of certain Organic Salts of Tellurium. AARON M. HAGEMAN (*J. Amer. Chem. Soc.*, 1919, **41**, 342—346).—Tellurium hydrogen tartrate is formed by heating at 70° tellurium dioxide with a solution of tartaric acid for several months. The solution may not be boiled, for a quantity of tellurium is thereby separated. Since the tartrate cannot be separated from tartaric acid by crystallisation, it is necessary to use the exact quantities required in the preparation. The pure salt has the formula $Te(HC_4H_4O_6)_4$. Tellurium hydrogen citrate, $Te(HC_6H_5O_7)_2$, is formed as a white, opaque, crystalline compound which separates in radiating clusters. It is produced by boiling tellurium dioxide with an aqueous solution of citric acid for a month. This compound does not deposit tellurium on boiling, and may be separated from citric acid by crystallisation. Succinic acid does not attack tellurium dioxide. Solutions of oxalic, lactic, malic, and gallic acids hold appreciable quantities of tellurium dioxide in solution, but it was found impossible to separate a crystalline compound of tellurium with any of these acids from solution. It is possible that an oleate and stearate of tellurium exist, but a pure, crystalline compound could not be obtained by the action of tellurium tetrachloride in benzene on a benzene solution of copper oleate or stearate.

J. F. S.

Polymerisation of Formaldehyde by Alkalis. C. MANNICH (*Ber.*, 1919, **52**, [B], 160--162).—By keeping 30% formaldehyde solution (almost free from methyl alcohol) containing 1--4% of anhydrous sodium carbonate, 0.3% of sodium hydroxide or 0.3% of calcium oxide for four months, crystals, the separation of which begins within one day, are obtained, which prove to be α -polyoxymethylene (Auerbach and Barschall, A., 1908, i, 131). The yield, which is 43% of the theoretical in the best case (with 4% of sodium carbonate), is diminished if methyl or ethyl alcohol is present. C. S.

Improvements in the Manufacture of Diethyl and Dimethyl Ketones. NEVIL VINCENT SIDGWICK and BERTRAM LAMBERT (Brit. Pat., 14085 of 1915).—A practically quantitative yield of acetone or of diethyl ketone may be obtained by passing the vapour of acetic or propionic acid over manganous oxide at 350°. The process may be carried out either with or without the dilution of the acid with water, and an acid diluted to 20% may be used. The catalyst is prepared by boiling pumice stone in a strong aqueous solution or suspension of manganous acetate or carbonate, and continuing the boiling until all the water is evaporated, the temperature not being allowed to rise above 200° unless air is excluded. W. G.

Action of Neutral Salts on the Inversion of Sucrose by Acids. H. COLIN and M. LEBERT (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 14--17).—A study of the inhibitive influence of sodium acetate, sodium citrate, and potassium oxalate on the hydrolytic action of the respective acids and on that of hydrochloric acid. The results are in accord with the known retrogression of the degree of electrolytic dissociation of weak acids in presence of their salts. [See *J. Soc. Chem. Ind.*, 1919, May.] J. H. L.

Transformations of Nitrocellulose. A. ANGELI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 20--24).—Nitrocellulose in the form of collodion cotton or guncotton is readily gelatinised by pyridine (compare Walter, A., 1911, i, 124), a large proportion of the latter yielding dense liquids which have the appearance of collodion, and gradually diminish in viscosity until, after a few days at the ordinary temperature, they resemble in this respect the pure pyridine; this phenomenon serves to detect unaltered cellulose in nitrocellulose. Treatment of the collodion cotton with just sufficient pyridine to moisten it yields a semi-solid, transparent mass with the appearance of caoutchouc, this also becoming continually more fluid until it is able to pass through filter paper. The yellow liquid thus formed smells strongly of pyridine, and with water gives an almost white mass, which has a resinous appearance and tenaciously retains pyridine. When freed from the latter by means of alcohol and dilute sulphuric acid, reprecipitated, washed, and dried over sulphuric acid, the product forms a white, amorphous powder, soluble readily in acetone and to a less extent

in alcohol, and almost insoluble in ether or benzene; the yield is about 80% of the collodion cotton used. The compound contains 9—10% of nitrogen, and somewhat resembles the substance obtained in small proportion by Berl and Fodor (A., 1911, i, 264) by treatment of very dilute alcoholic or ethereal solution of nitrocellulose with alkali hydroxide or sodium carbonate. It begins to turn brown at about 165°, and becomes almost black at 250°. When its alcoholic solution is poured into water, it forms a very stable, opalescent, colloidal solution, which is coagulated immediately by sodium chloride, ammonium sulphate, or gelatin solution, but is not precipitated by aqueous tannin solution. With benzene and sulphuric acid, it gives nitrobenzene, and with sulphuric acid in presence of mercury, nitric oxide. On a wet dimethylaminoazobenzene paper, it forms slowly an intensely red spot. It reduces ammoniacal silver nitrate and reacts readily with phenylhydrazine, but has no action on Fehling's solution. Quinoline and nicotine also act, but more slowly, on nitrocellulose.

T. H. P.

Origin of Creatine. III. KARL THOMAS and M. G. H. GOERNER (*Zeitsch. physiol. Chem.*, 1919, **104**, 73—87. Compare A., 1914, i, 353, 1110).—No increase in the urinary creatine was observed to follow the oral or subcutaneous administration of ϵ -methylguanidinohexoic acid or γ -methylguanidinobutyric acid to rabbits. The preparation of these acids and certain closely related compounds is described. *Toluenesulphonyl- ϵ -amino-*n*-hexoic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, crystallises from water in slender needles, m. p. 104—106°. *Toluenesulphonyl- ϵ -methylamino-*n*-hexoic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NMe}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, crystallises from water or ethyl acetate in white, slender needles, m. p. 55—59°. *ϵ -Methylamino-*n*-hexoic acid*, $\text{NHMe}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, crystallises with $1\frac{1}{2}$ molecules of water. The hydrated form melts indefinitely at 67°; the anhydrous form, crystallised from alcohol, melts at 132°.

ϵ -Methylguanidinohexoic acid, $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NMe}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, prepared from ϵ -methylamino-*n*-hexoic acid (ϵ -methyl-leucine) and cyanamide, crystallises with difficulty from water in microscopic tufts of needles. It decomposes without melting about 285°. The *hydrochloride* of this acid crystallises from alcohol in slender needles, m. p. 105°, and the *nitrate* melts indefinitely at 80—85°. For purposes of identification, the *acid oxalate* serves best. This salt crystallises from water in needles, m. p. 167—168° (uncorr.). *ϵ -Methylcarbamido-*n*-hexoic acid*, $\text{NH}_2\cdot\text{CO}\cdot\text{NMe}\cdot[\text{CH}_2]_5\cdot\text{CO}_2\text{H}$, crystallises from water in stout needles, m. p. 163° (decomp.). *Toluenesulphonyl- γ -aminobutyric acid*,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, m. p. 135°, crystallises from water. *Toluenesulphonyl- γ -methylaminobutyric acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NMe}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, m. p. 96—98°, crystallises from dilute alcohol. γ -Methylaminobutyric acid is very hygroscopic. *γ -Methylguanidinobutyric acid*,

$\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NMe}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$,

was not obtained in the pure condition. γ -Carbamidobutyric acid, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, m. p. 175–176° (decomp.), crystallises from water or alcohol. J. C. D.

Bromination of Unsaturated Compounds with *N*-Bromoacetamide. The Law of the Course of Chemical Reactions.

A. WOHL (*Ber.*, 1919, **52**, [B], 51–63).—In the presence of cold acetone or ethyl ether as solvent, acetobromoamide reacts with certain substances as a brominating agent, acetamide being produced, but not hydrogen bromide. Thus *tert*.-butyl bromide is converted into *isobutylene* dibromide, phenol into *p*-bromophenol, anisole into *p*-bromoanisole, ethyl acetoacetate into ethyl α -bromoacetoacetate, and the half-amide of malonic ester into the half-amide of bromomalonic ester. $\beta\gamma$ -Dimethyl- Δ^{β} -butene yields α -bromo- $\beta\gamma$ -dimethyl- Δ^{β} -butene amongst other products. β -Methyl- Δ^{β} -butene in ethereal solution yields dibrominated and more highly brominated products, but in acetone solution with 2 mols. of acetobromoamide it yields an unsaturated dibromo-derivative. In acetone solution, γ -bromo- β -methyl- Δ^{β} -butene can be further brominated by acetobromoamide, and yields an unsaturated dibrominated product.

In the reactions between acetobromoamide and the preceding unsaturated compounds, there is no addition of fragments of the acetobromoamide molecule at the double linking, but the whole molecule must become attached to one of the carbon atoms by residual affinity; an interchange of hydrogen and bromine occurs between the two molecules, and acetamide and a bromine-substituted derivative of the unsaturated compound are produced.

C. S.

Mercury Fulminate and some of its Impurities. PAUL

NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1919, [iv], **25**, 119–122).—Sodium and ammonium thiosulphates in 5% aqueous solutions are much more satisfactory solvents than potassium cyanide at the same concentration for analytical purposes, since they do not dissolve the impurities likely to be present in the fulminate, whilst these are soluble in the potassium cyanide solution. Heaven's method (*A.*, 1918, ii, 233) for the estimation of mercury fulminate may be applied to the extract made with either of the thiosulphates. For the method of recovery of mercury from the residues in the manufacture of mercury fulminate, see *J. Soc. Chem. Ind.*, 1919, May. W. G.

Organic Fluorine Compounds. III. I. J. RINKES (*Chem.*

Weekblad, 1919, **16**, 206–213).—The assertion of Meyer and Hub (*A.*, 1910, i, 735) that by means of the Hoffmann reaction no fluoroaniline is obtained from *o*-fluorobenzamide is disproved, the reaction being, on the contrary, an excellent preparative method giving good yields of fluoroaniline. *o*-Fluorobenzamide was prepared from *o*-toluidine by diazotising in presence of hydrofluoric

acid. The oxidation of the *o*-fluorotoluene is effected by the chlorination of the methyl group and subsequent hydrolysis, which permits of the preparation of the aldehyde. This method is preferable to the direct oxidation by means of permanganate. *p*-Fluorobenzaldehyde was prepared in a similar way, and with hydroxylamine hydrochloride and sodium carbonate gives directly *p*-fluoroantialdoxime (m. p. 81·2°). Regeneration of the oxime from the hydrochloride by means of sodium carbonate gives *p*-fluorosynaldoxime (m. p. 116—117°). *o*-Fluorobenzaldoxime hydrochloride on treatment with sodium carbonate yields the original antialdoxime. This behaviour is analogous to that of *o*- and *p*-chlorobenzaldoximes.

o-Fluoroiodobenzene, b. p. 188·6°/759 mm., was prepared from *o*-fluoroaniline by diazotising and adding potassium iodide.

p-Fluoroiodobenzene, b. p. 183·2°/760 mm., was prepared in a similar way. This was obtained in two crystalline forms, m. p. -27·2° and -18° respectively.

An attempt to prepare fluorine derivatives of iodobenzene with fluorine in the nucleus was unsuccessful: Phenyl iododifluoride was first prepared from iodosobenzene and fuming hydrofluoric acid. This was kept for three months in a copper tube. No formation of fluoroiodobenzene was observed, the principal product being apparently diphenyl.

p-Fluoronitrosobenzene was prepared from *p*-fluoroaniline by oxidation by means of ammonium persulphate, and its behaviour studied with respect to condensation in concentrated sulphuric acid. The chief condensation product was found to be 2:7-difluorophenazine-5:10-oxide, brownish-yellow needles, m. p. 150°, analogous to the corresponding chlorine derivative obtained by Bamberger and Ham (A., 1911, i, 684).

W. S. M.

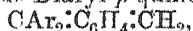
Catalytic Dehydrogenation by Nickel in the Presence of Hydrogen. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1919, 168, 670—672).—Hydrocarbons of the benzene series when passed with hydrogen over nickel at 180° undergo hydrogenation, but if the temperature is raised to 350—360°, dehydrogenation occurs. Thus at this higher temperature pinene yields a mixture of cymene and cumene; limonene and camphene yield the same mixture; menthene gives cymene; cyclohexene gives benzene; cyclohexanol gives phenol; pulegone gives a mixture of cresol and thymol; eucalyptol, terpene, and terpineol undergo dehydration as well as dehydrogenation. The presence of hydrogen is essential for this dehydrogenation.

W. G.

Formation and Stability of spiro-Compounds. II. Bridged-spiro-compounds Derived from cyclo-Hexane. CHRISTOPHER KELK INGOLD and JOCELYN FIELD THORPE (T., 1919, 115, 320—333).

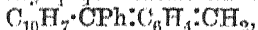
Solubilities, Separation, and Purification of Anthracene, Carbazole, and Phenanthrene. JOHN MARSHALL CLARK (*J. Ind. Eng. Chem.*, 1919, **11**, 204—209).—Various solvents have been proposed for separating anthracene, carbazole, and phenanthrene from the "anthracene oil" of coal tar, but none effects complete separation, and chemical methods are required to complete the purification. At 15.5° , benzene dissolves 1.04% of anthracene, 0.72% of carbazole, and 16.72% of phenanthrene; acetone dissolves 0.55% of anthracene, 6.12% of carbazole, and 15.08% of phenanthrene; and light pyridine, 0.85%, 12.45%, and 25.54% of the respective substances. In the method described, crude coal-tar solvent naphtha is used to remove the phenanthrene, and pyridine to separate carbazole from anthracene. The anthracene is then purified by fusion with alkali, to retain the carbazole and sublimation, whilst carbazole is purified by treatment with 98% sulphuric acid, which combines with anthracene to form a sulphonated compound soluble in a large volume of water, whilst the carbazole is scarcely affected. In the fusion with alkali, the best results are obtained by the use of a mixture of potassium and sodium hydroxides. [See, further, *J. Soc. Chem. Ind.*, 1919, 247A.] C. A. M.

***p*-Quinodimethanes.** W. SCHLENK and EGON MEYER (*Ber.*, 1919, **52**, [B], 8—21).—*as*-Diaryl-*p*-quinodimethanes,



have now been prepared, essentially by Tschitschibabin's method (A., 1908, i, 872), but in some cases the product is difficult (or impossible) to isolate on account of its tendency to polymerise. Thus, *as*-diphenyl-, *as*-phenyl-*p*-tolyl-, and *as*-phenyldiphenylquinodimethanes could not be isolated, and *as*-di- α -naphthylquinodimethane could only be obtained in solution.

By keeping at the ordinary temperature, or more rapidly by warming, a solution of phenyl-*p*-tolyl α -naphthylchloromethane in pyridine with the complete exclusion of air and in the absence of light, *as*-phenyl- α -naphthyl-*p*-quinodimethane,



is obtained. Its isolation is difficult, but the substance is ultimately obtained as a dark blue powder. Its solutions are intensely bluish-violet, and in the dilute state exhibit a green fluorescence. Its ethereal solution is instantly decolorised by oxygen, chlorine, bromine, or ferric chloride. The tendency to polymerise is relatively small, but it does polymerise, frequently without obvious cause.

In a similar manner, phenyl-*o*-tolyl-*p*-tolylchloromethane yields *as*-phenyl-*o*-tolyl-*p*-quinodimethane, $\text{C}_7\text{H}_7\cdot\text{CPh}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2$, violet powder, which is somewhat more stable than the preceding compound towards oxygen.

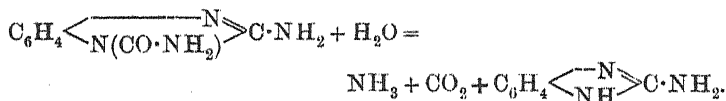
The intense colour of these two diarylquinodimethanes in comparison with that of tetra-arylquinodimethanes is very remarkable; also in solution they exhibit selective absorption in the visible

spectrum, whereas the tetra-aryl compounds show continuous absorption.

Phenyl-p-tolyl-α-naphthylcarbinol, $C_{10}H_7 \cdot CPh(C_7H_7) \cdot OH$, prepared in the usual way from magnesium α-naphthyl bromide and phenyl p-tolyl ketone, is a colourless, crystalline powder, m. p. 109—110°, which is converted by hydrogen chloride in ethereal solution into *phenyl-p-tolyl-α-naphthylchloromethane*, m. p. 142—144°. *Phenyl-o-tolyl-p-tolylchloromethane*, prepared in a similar manner, has m. p. 86·5°. *Phenyl-o-tolyldiphenylcarbinol*, colourless crystals, m. p. 137—138°, and the *chloride*, $C_6H_4Ph \cdot CPhCl \cdot C_7H_7$, m. p. 161°, are described. *p-Tolyldi-α-naphthylcarbinol* could not be isolated in a pure state, since by repeated crystallisation it is changed to *p-tolyldi-α-naphthylfluorene*, $\begin{matrix} C_{10}H_6 \\ C_{10}H_6 \end{matrix} > C(OH) \cdot C_7H_7$, needles, m. p. 162·5—163°.

C. S.

o-Aminophenylcarbamide. GUIDO PELLIZZARI (*Gazzetta*, 1919, 49, i, 16—26).—This compound, prepared by a method simpler than that used by Schiff and Ostrogovich (*A.*, 1897, i, 144) for its meta- and para-isomerides, has basic properties, and treatment of its hydrochloride with potassium cyanate yields *o*-phenylenedicarbamide. At 150°, it loses quantitatively 1 mol. of ammonia, giving *o*-phenylenecarbamide, which is prepared most simply in this way. Treatment of *o*-phenylenediamine with cyanogen bromide yields *o*-phenyleneguanidine, but in the case of *o*-amino-phenylcarbamide, this reagent gives first *o*-cyanoaminophenylcarbamide, which is an acid compound stable in dry air, but is gradually changed by moist air or by water into the metameric basic compound, *o*-phenylene-α-guanylcabamide. The latter cannot be obtained pure in the free state, since it is hygroscopic and tends to undergo hydrolysis into *o*-phenyleneguanidine, ammonia, and carbon dioxide:



This decomposition, which occurs slowly in the cold and more rapidly in the hot, is greatly accelerated by the presence of either alkali or mineral acid. Thus the salts of *o*-phenylene-α-guanylcabamide could not, in general, be prepared, although the action of picric acid on cold aqueous *o*-cyanoaminophenylcarbamide yields the picrate, which is decomposed similarly by hot water, *o*-phenyleneguanidine picrate crystallising out from the solution.

The existence of this highly unstable *o*-phenylene-α-guanylcabamide confirms the constitutional formulæ attributed to the two cyano-derivatives described previously (this vol., i, 134).

o-Aminophenylcarbamide, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, prepared by the action of potassium cyanate (1 mol.) on *o*-phenylenediamine

L.*

monohydrochloride (1 mol.), forms shining needles, and shows signs of melting at 175° , then becomes opaque, and melts at 307° ; in a moist atmosphere, it has m. p. 175° (decomp.), a solid residue, m. p. 307° , which is that of *o*-phenylenecarbamide, remaining. Its *picrate*, $C_7H_5ON_3 \cdot C_6H_3O_7N_3$, forms an almost gelatinous, felted mass of long, very slender needles, decomposing at $200-235^{\circ}$. The *nitrate*, $C_7H_5ON_3 \cdot HNO_3 \cdot \frac{1}{2}H_2O$, long, white needles, reddens at $170-175^{\circ}$, and then contracts and undergoes gradual alteration. The hydrochloride and platinichloride crystallise well and are moderately soluble.

o-Cyanoaminophenylcarbamide, $CN \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot NH_2$, forms small, white, shining crystals, and decomposes at 110° .

o-Phenylene- α -guanilycarbamide *picrate*, $C_8H_8ON_4 \cdot C_6H_3O_7N_3$, forms a yellow powder and decomposes at $250-260^{\circ}$. T. H. P.

Compounds of Phenols, Phenolic Ethers, and Salicylaldehyde with Normal Salts. R. F. WEINLAND and GUSTAV BÄRLOCHER (*Ber.*, 1919, 52, [B], 147-159).—An extension of the work of Weinland and Denzel (*A.*, 1914, i, 953; 1915, i, 526). *Compounds* of the type $CaX_2 \cdot 4C_6H_4(OH)_2 \cdot 2R \cdot OH$ have been obtained, where X is Cl, Br or I, and R is Me, Et, Prⁿ, or C_6H_{11} , from solutions of catechol and the calcium haloid (anhydrous) in the respective alcohols; they all form colourless crystals which are stable over sulphuric acid. Quinol forms similar compounds, but less readily, whilst resorcinol does not.

Quinol forms *compounds*, colourless crystals, with potassium formate, acetate, and propionate, $H \cdot CO_2K \cdot 2C_6H_4(OH)_2$,

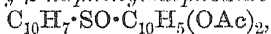
$2CH_3 \cdot CO_2K \cdot 3C_6H_4(OH)_2$, and $C_2H_5 \cdot CO_2K \cdot 2C_6H_4(OH)_2$. Pyrogallol forms *compounds*, $KA \cdot C_6H_3(OH)_3$, with the same three salts, whilst phloroglucinol forms the *compound* $CH_3 \cdot CO_2K \cdot C_6H_3(OH)_3$. All these compounds crystallise from alcoholic solutions of the components.

Compounds, colourless, stable crystals, have been obtained from guaiacol (2 mols.) and potassium formate, acetate, propionate or butyrate (1 mol.), guaiacol (2 mols.) and sodium acetate (1 mol.), eugenol (2 mols.) and potassium propionate (1 mol.), vanillin (1 mol.) and potassium propionate (1 mol.), vanillin (3 mols.) and potassium acetate, propionate or butyrate (2 mols.), and vanillin (2 mols.) and potassium formate or sodium acetate (1 mol.).

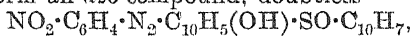
Compounds, pale yellow, stable needles, have been obtained from alcoholic solutions of salicylaldehyde (2 mols.) and potassium acetate, propionate or butyrate (1 mol.). C. S.

Derivatives of *iso*- α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone. O. HINSBERG (*Ber.*, 1919, 52, [B], 28-35).—An instance of stereoisomerism analogous to that of the β -naphthol sulphides is described. α -Naphthyl-1:4-dihydroxy- β -naphthylsulphone (*A.*, 1917, i, 575) undoubtedly belongs to the normal series of sulphones. By heating at 170° , it loses 1 mol. of water, and is converted into a *substance*, brownish-red, crystalline powder, sintering at 85° and

completely molten at 105° , which undoubtedly has the formula $C_{10}H_7 \cdot SO \cdot C_{10}H_5O_2$, and, on account of its ready solubility, low and indefinite m. p., and intense colour, belongs to the *iso*-series, and is therefore *iso- α -naphthyl-2- α -naphthaquinonylsulphoxide* (two by-products are formed in this reaction, the one a grey, very sparingly soluble substance, the other, yellow crystals, m. p. 225° [decomp.]). The *iso*-sulphoxide is reduced and acetylated by zinc dust and acetic anhydride on the water-bath, yielding *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphoxide*,



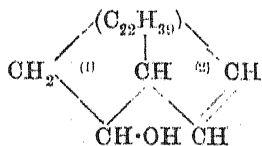
pale yellow, crystalline powder containing $\frac{1}{2}CHCl_3$ (from chloroform), decomp. 73° and completely molten at 105° . The *iso*-sulphoxide combines with *p*-nitrophenylhydrazine in warm glacial acetic acid to form an *azo*-compound, doubtless



red powder, and is oxidised in warm glacial acetic acid solution by 30% hydrogen peroxide, yielding *iso- α -naphthyl-2- α -naphthaquinonylsulphone*, $C_{10}H_7 \cdot SO_2 \cdot C_{10}H_5O_2$, yellowish-brown needles or crusts containing $\frac{1}{2}H_2O$, m. p. 110 — 115° (decomp.), which is quite different from the isomeric *α -naphthyl-2- α -naphthaquinonylsulphone* (*loc. cit.*), exhibits its quinone nature by reacting with aniline and with *p*-nitrophenylhydrazine, and is reduced and acetylated by zinc dust and acetic anhydride, yielding a colourless substance, probably *iso- α -naphthyl-1:4-diacetoxy- β -naphthylsulphone*.

C. S.

Cholesterol. XXVI. Ring Systems in Cholesterol. A. WINDAUS and O. DALMER (*Ber.*, 1919, 52, [B], 162—169).—Investigations demonstrative of the number of atoms in the two ring systems of the cholesterol molecule (Windaus, A., 1917, i, 265) have not hitherto been undertaken. The authors attack the problem as follows.

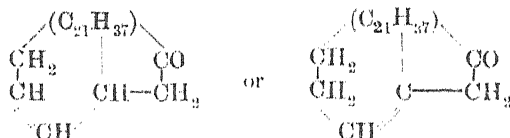


By hydrogenation at the double linking (annexed formula), ring 2 is rendered proof against oxidation, and ring 1 is then ruptured; if, on the other hand, the hydroxyl group in ring 1 is replaced by hydrogen, ring 2 is then ruptured on oxidation. In both cases, dicarboxylic acids are obtained, in which the positions of the carboxyl groups are determined with great probability by Blanc's method with acetic anhydride (A., 1907, i, 710).

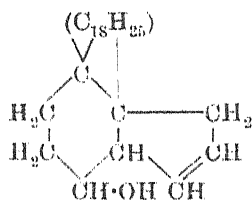
Dihydrocholesterol (β -cholestanol), obtained by reducing cholesterol in acetic acid solution at 100° with hydrogen and palladium, is oxidised to the dicarboxylic acid, $C_{27}H_{46}O_4$ (Windaus and Ubrig, A., 1914, i, 1066). By heating with acetic anhydride until the reagent has distilled completely, and then at $250^{\circ}/15$ — 20 mm., this acid is converted into a *ketone*, $C_{26}H_{44}O$, leaflets, m. p. 100 — 100.5° (*oxime*, needles, m. p. 203°), which is oxidised by glacial acetic and nitric (D 1.48) acids at 75 — 80° to a dibasic acid, $C_{26}H_{44}O_4$, needles, m. p. 234 — 235° . This acid, by treatment

with acetic anhydride and subsequent heating in a vacuum, yields its *anhydride*, $C_{26}H_{42}O_3$, crystals, m. p. 153° . The carboxyl groups in this acid, therefore, are in the 1:5-positions, those in the acid $C_{27}H_{46}O_4$ are in the 1:6-positions, and ring 1 of the cholesterol molecule contains six atoms of carbon.

Cholestene did not prove a suitable material for the rupture of ring 2, since it did not yield the desired dicarboxylic acid on oxidation. Therefore α -chlorocholestanone in alcoholic solution was converted by 20% potassium hydroxide at 50° into *heterocholestenone*,



needles, m. p. 96° , which was reduced in glacial acetic acid solution by hydrogen and palladium to *heterocholestanone*, $C_{27}H_{46}O$, leaflets, m. p. $98-99^\circ$ (*oxime*, needles, m. p. 195°). The latter ketone, which can also be obtained by reducing nitrocholestene with zinc dust and acetic acid, and yields cholestane by reduction by Clemmensen's method, is converted by glacial acetic and nitric (D 1.48) acids at $70-75^\circ$ into a dibasic acid, $C_{27}H_{46}O_4$, needles, m. p. 273° (decomp.), which yields its *anhydride*, $C_{27}H_{44}O_3$, needles, m. p. 118° , by treatment with acetic anhydride and subsequent distillation in a vacuum. The carboxyl groups in the acid $C_{27}H_{46}O_4$, therefore, are in the 1:4- or 1:5-positions. Only the latter alternative is permissible, and ring 2 there-



fore contains five atoms of carbon. On the assumption, therefore, that Blanc's method gives trustworthy results in the case of complicated cyclic structures, the constitution of the cholesterol molecule has been elucidated to the extent indicated in the annexed formula.

C. S.

Cholesterol. XXVII. Isomerism of Cholestane and ψ -Cholestane. A. WINDAUS (*Ber.*, 1919, 52, [B], 170--176. Compare preceding abstract).—Cholestane is without doubt the normal dihydro-derivative of cholestene. ψ -Cholestene, which yields ψ -cholestane by reduction in ethereal solution by hydrogen and platinum (Mauthner, A., 1907, i, 921; 1909, i, 714), is now found to give cholestane almost exclusively when reduced in glacial acetic acid solution by hydrogen and palladium at 75° . Cholestene and ψ -cholestene, therefore, differ only in the position of the double linking. ψ -Cholestane can therefore very well be a diastereoisomeride of cholestane, ring 2 (*loc. cit.*) being affixed to ring 1 in the *cis*-position. Some experimental observations support the new formulation. Dihydrocholesterol, derived from cholestane, is con-

verted through the acid $C_{27}H_{46}O_4$ into the ketone $C_{26}H_{44}O$ (*loc. cit.*). Coprosterol, derived from ψ -cholestane, yields by oxidation the isomeric acid $C_{27}H_{46}O_4$, which by evaporation with acetic anhydride and subsequent distillation in a vacuum is converted into an isomeric *ketone*, $C_{26}H_{44}O$, needles, m. p. 73—74°. The very smooth course of the ketone formation indicates that the two carboxyl groups in the two isomeric acids are in the *cis*-position. The acid $C_{27}H_{44}O_4$ obtained from cholesterol by Diels and Abderhalden (A., 1904, i, 880) is reduced in glacial acetic acid solution at 100° by hydrogen and palladium to a third isomeric *acid*, $C_{27}H_{46}O_4$, leaflets, m. p. 252° (*methyl ester*, $C_{26}H_{50}O_4$, prisms, m. p. 123—124°), which is converted by the acetic anhydride method, although far less smoothly, into the ketone, $C_{26}H_{44}O$, obtained from coprosterol through the second isomeric acid $C_{27}H_{46}O_4$. It is extremely probable, therefore, that the two acids $C_{27}H_{46}O_4$ last mentioned only differ from one another in that the two carboxyl groups in the former (which is less readily converted into the ketone) are in the *trans*-position, and in the latter are in the *cis*-position.

C. S.

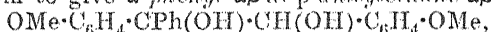
Molecular Transpositions of α -Glycols. II. Product of Dehydration of $\alpha\beta\gamma$ -Triphenylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 108—111. Compare this vol., i, 146).—Magnesium benzyl chloride condenses with benzoin to give $\alpha\beta\gamma$ -triphenylpropan- $\alpha\beta$ -diol, $CH_2Ph \cdot CPh(OH) \cdot CHPh(OH)$, m. p. 159—160°, giving a *monoacetyl* derivative, m. p. 176—177°. The glycol, when dehydrated with sulphuric acid, yields *benzyl diphenylmethyl ketone*, $CHPh_2 \cdot CO \cdot CH_2Ph$, m. p. 80—81°, giving an *oxime*, m. p. 134—135°, and a *phenylhydrazone*, m. p. 99—100°. This ketone, when heated with alcoholic potassium hydroxide, is decomposed, giving diphenylmethane and potassium phenylacetate, and when condensed with magnesium benzyl chloride yields $\beta\beta$ -diphenyl- $\alpha\alpha$ -dibenzylethyl alcohol, $CHPh_2 \cdot C(C_6H_5)_2 \cdot OH$, m. p. 92—93°, which is also obtained by condensing ethyl diphenylacetate with magnesium benzyl chloride.

W. G.

Molecular Transpositions of α -Glycols. III. The Dehydration of $\alpha\gamma$ -Diphenyl- β -benzylpropan- $\alpha\beta$ -diol. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 111—115. Compare preceding abstract).—[With J. ZIRN.]—Magnesium benzyl chloride condenses with methyl phenylglycollate to give $\alpha\gamma$ -diphenyl- β -benzylpropan- $\alpha\beta$ -diol, $CHPh(OH) \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 110—111°, giving a *monoacetyl* derivative, m. p. 125—126°. The glycol, when dehydrated with sulphuric acid, yields *benzyl $\alpha\beta$ -diphenylethyl ketone*, $CH_2Ph \cdot CHPh \cdot CO \cdot CH_2Ph$, m. p. 75—76°, giving an *oxime*, m. p. 77—78°, and a *phenylhydrazone*, m. p. 126—127°. This ketone condenses with magnesium benzyl chloride to give $\alpha\beta\delta$ -triphenyl- γ -benzylbutan- γ -ol, $CH_2Ph \cdot CHPh \cdot C(CH_2Ph)_2 \cdot OH$, m. p. 122—123°, identical with the product obtained by the action of magnesium benzyl bromide on methyl $\alpha\beta$ -diphenylpropionate.

W. G.

Molecular Transpositions of the α -Glycols. IV. Product of Dehydration of a Methoxy-derivative of $\alpha\beta\beta$ -Triphenyl ethanediol. Phenyl Migration. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 115—118. Compare preceding abstract).—[With F. COMA-Y-ROCA.]—Magnesium phenyl bromide condenses with *p*-anisoin to give α -phenyl- $\alpha\beta$ -di-*p*-anisylethane- $\alpha\beta$ -diol,



m. p. 163—164°, which when dehydrated with sulphuric acid yields phenyldi-*p*-anisylacetaldehyde, $\text{CHO} \cdot \text{CPh}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$, m. p. 88—89°, giving an oxime, m. p. 132—133°, and a semicarbazone, m. p. 186—187°. This aldehyde is decomposed by alcoholic potassium hydroxide, giving phenyldi-*p*-anisylmethane, m. p. 100—101° (compare Feuerstein and Lipp, A., 1902, i, 768).

W. G.

β -Bromoethyl *p*-Nitrobenzoate. THE ABBOTT LABORATORIES, (Brit. Pat., 121578).—The β -bromoethyl ester of *p*-nitrobenzoic acid is prepared by heating a salt of *p*-nitrobenzoic acid with an excess of ethylene bromide, preferably in the presence of an amine or of finely divided copper as a catalyst. A mixture of 15 grams of the dry sodium salt, 75 grams of ethylene bromide, and 0.5—1.0 c.c. of diethylamine is heated in a sealed tube at 140° for five hours. The product is neutralised, the excess of ethylene bromide is removed by distillation with steam, and the residue of β -bromoethyl *p*-nitrobenzoate is separated from a small quantity (about 4 grams) of the di-*p*-nitrobenzoic ester of ethylene glycol, which is formed as a by-product, by means of a suitable solvent, such as ether. The yield of crude product is about 15 grams; the pure β -bromoethyl ester has m. p. 51—52°, and may be converted into novocaine (diethyl-aminoethyl *p*-aminobenzoate) by combination with diethylamine and reduction of the nitro-group.

J. F. B.

Application of Acetylated Phenolcarboxylic Acids to the Synthesis of Depsides. EMIL FISCHER and A. REFIK KADISADÉ (*Ber.*, 1919, 52, [B], 72—77).—Acetylated phenolcarboxylic acids can be used instead of the methylcarbonato-derivatives for the synthesis of the simpler depsides, but the advantages of the new method over the old are not so marked as in the case of the synthesis of digallic acid (A., 1918, i, 172). 4-*p*-Acetoxybenzoyloxybenzoic acid, $\text{OAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, microscopic needles or long leaflets, m. p. 221—223° (corr.) with previous sintering, is precipitated in the form of its sodium salt when an ethereal solution of *p*-acetoxybenzoyl chloride and aqueous sodium hydroxide are added gradually, with cooling, to a solution of *p*-hydroxybenzoic acid in aqueous sodium hydroxide (1 mol.). In a similar way, 4-*p*-hydroxybenzoyloxybenzoic acid is converted into the acetylated tridepside, and *p*-hydroxybenzoic acid and triacetyl-galloyl (triacetoxymethyl) chloride yield *p*-triacetoxymethyl-

benzoic acid, $\text{C}_6\text{H}_5(\text{OAc})_3 \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, microscopic leaflets, m. p. $172\text{--}173^\circ$ (corr.). C. S.

The Products of the Addition of Benzilic Acid to Aryl Thiocarbimides. H. BECKER and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, 2, 111—117).—In an earlier paper (A., 1915, i, 245), it was shown that benzilic acid and phenylthiocarbimide react to form *N*-phenyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid. The three *N*-tolyl derivatives, $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, have now been obtained from the tolylthiocarbimides in the same way, the yields being excellent; the *ortho*-derivative forms colourless tablets, decomp. 139° , the *meta*-compound decomposes at 141° , and the *para*- at $138\cdot5^\circ$.

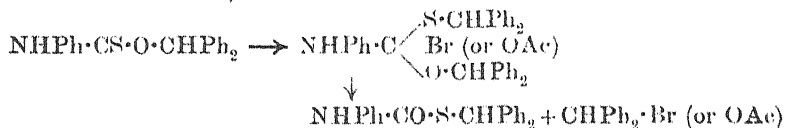
These acids readily lose carbon dioxide when heated at $60\text{--}100^\circ$ with pyridine, the products being the *S*-benzhydryl *N*-arylthiocarbamates, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$. The *phenyl* derivative forms bundles of needles, m. p. $135\text{--}136^\circ$; the *o*-tolyl compound crystallises in long needles, m. p. $123\cdot5\text{--}124\cdot5^\circ$; the *m*-tolyl compound forms glistening leaflets, m. p. $101\text{--}102\cdot5^\circ$; and the *p*-tolyl derivative forms long prisms, m. p. $149\cdot5\text{--}151^\circ$.

When the acids are boiled with methyl alcohol and concentrated sulphuric acid, they yield internal anhydrides, namely, the 5 : 5-diphenyl-3-arylthiazolid-2 : 4-diones, $\text{S} \begin{smallmatrix} \text{CO} \text{---} \text{NAr} \\ \text{CPh}_2 \text{---} \text{CO} \end{smallmatrix}$, as follows: the 3-phenyl derivative, long, glistening prisms, m. p. $147\cdot5\text{--}148\cdot5^\circ$; the *o*-tolyl compound, large, granular masses of hexagonal prisms, m. p. $108\text{--}109^\circ$; the *m*-tolyl compound, rectangular prisms, m. p. $96\cdot5\text{--}97\cdot5^\circ$; the *p*-tolyl compound, flat needles, m. p. $105\cdot5\text{--}106\cdot5^\circ$.

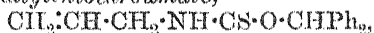
Benzilic and thiobenzilic acids react with undiluted phenylcarbimide at 100° to form *s*-diphenylcarbamide. It is reported that this substance suffers decomposition to a certain extent when melted (at about 234°) or distilled (about 260°). J. C. W.

Transformations of some O-Esters of Arylated or Alkylated Thiocarbamic Acids. A. BETTSCHART and A. BISTRZYCKI (*Helv. Chim. Acta*, 1919, 2, 118—132).—In their first communication on the condensation of benzilic acid with arylthiocarbimides in the presence of pure acetic and sulphuric acids (A., 1915, i, 245), Becker and Bistrzycki offered an explanation of the mechanism of the unusual reaction, which has now been tested and found to be justified. They assumed that the first product was the expected *O*-ester, $\text{NHAr} \cdot \text{CS} \cdot \text{O} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$. Attempts to isolate such esters have failed, but closely related substances, with which the theory can be tested, have now been obtained by the action of the thiocarbimides on the sodium compound of benzhydrol dissolved in xylene. These esters may be transformed readily into the *S*-esters, $\text{NHAr} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, by boiling with glacial acetic acid, although in the case of the phenyl compound many other methods have been found, including heating at

130—135°, or treatment with cold hydrochloric acid. The transformations by means of acids are explained by assuming that a little benzhydrol is liberated by hydrolysis, and is then attached at the $-C:S$ group in the form of its acetate or chloride, which is then eliminated again from the other position. Theoretically, therefore, a trace of such an ester should cause the transformation of an unlimited amount of *O*-ester into *S*-ester, and the whole theory is neatly proved by the fact that the change can indeed be brought about by heating with a small quantity of benzhydryl acetate or bromide in toluene, thus:



The following *O*-benzhydryl *N*-arylthiocarbamates are described; their isomerides have been made in the above manner, but are also mentioned in the previous abstract: The *phenyl* derivative, quadratic prisms, m. p. 123—123·5°; the *o*-tolyl compound, m. p. 123·5—124° (decomp.); and the *p*-tolyl compound, decomp. 126·5°. *O*-Benzhydryl *N*-allylthiocarbamate,

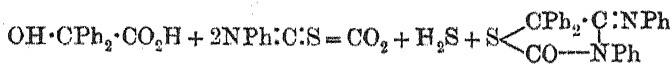


has also been prepared, in quadratic prisms, m. p. 59·5—61·5°, and converted into the *isomeride*, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CHPh}_2$, which forms very long prisms, m. p. 114·5—116·5°.

This transformation seems to depend on the nature of the group which wanders, for the benzyl derivative, $\text{NHPh} \cdot \text{CS} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$, is not so changed by acetic acid.

Benzilic acid will not condense with alkylthiocarbimides under the conditions employed in the earlier cases, but if phosphoric oxide is added as well as sulphuric acid, the same kind of reaction takes place. Ordinary mustard oil gives *N*-allyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{S} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, prisms, decomp. about 133°, which is quantitatively converted into α -thioldiphenylacetic acid by boiling with 1% potassium hydroxide (a more convenient preparation than the earlier one, *loc. cit.*), or may be changed into the above *S*-benzhydryl *N*-allylthiocarbamate by heating with pyridine. *N*-isoButyl-*S*-benzhydrylthiocarbamate- α -carboxylic acid, rhombic tablets, m. p. 123—124° (decomp.), and *S*-benzhydryl *N*-isobutylthiocarbamate, long, silky prisms, m. p. 73·5—75°, have also been obtained.

In the hope of getting a normal *O*-ester from benzilic acid and phenylthiocarbimide, these substances have been heated together without diluents at 100°. A reaction, represented by the equation



was found to take place, the product being 4-phenylimino-3:5:5-triphenylthiazolid-2-one, which crystallises in prisms, m. p.

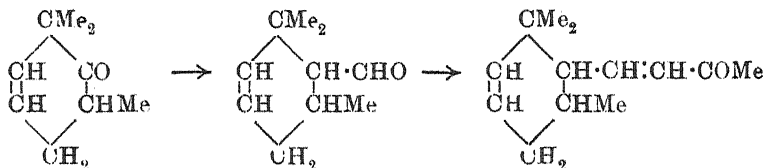
162.5—163.5°, and yields the 3:5:5-triphenylthiazolid-2:4-dione, mentioned in the previous abstract, when boiled with acetic and sulphuric acids.

J. C. W.

Preparation of Benzaldehyde. THE DOW CHEMICAL COMPANY (U.S. Pat., 1272522).—Benzyl bromide is mixed with a solution of sodium nitrate or calcium nitrate, and the mixture is heated at about the boiling point with constant agitation; the benzaldehyde produced is then separated from the aqueous solution of sodium bromide and nitrous acid. The reaction takes place between equimolecular proportions of benzyl bromide and sodium nitrate, and the benzaldehyde is practically a pure product, whereas that produced with benzyl chloride and lead nitrate is always contaminated with benzoic acid.

J. F. B.

Preparation of Polymethylcyclohexenones of the Irone Type. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 144—161).—For the synthesis of perfumes of the type of irone, the author argues that it is important to start from compounds in which the ethylene linking in the cyclohexene ring is already fixed, such methods as those described by Merling and Velde, for example (A., 1909, i, 479), being open to question on this point. The conversion of a cyclohexenone of the desired type into irone or a similar compound would be quite a simple matter; thus:



The present communication describes the preparation of two such cyclohexenones, but the yields are so poor that further developments along these lines seem to be useless.

The desired cyclohexenones should be most readily obtained from the corresponding unsaturated dicarboxylic acids, and these from δ -ketonic esters by Reformatsky's method. The chief obstacle is the closing of the ring in the case of the dicarboxylic esters. Two examples are given.

A. Preparation of the δ -Ketonic Esters.— δ -Ketohectic acid may be prepared most readily by the interaction of ethyl sodioacetate and ethyl β -iodopropionate. With suitable apparatus, it may also be obtained by heating dihydroresorcinol with barium hydroxide and water at 150°. A third method, giving poor results, is as follows: fresh ethyl methylenemalonate is treated with ethyl sodioacetate solution at 0°, and the ethyl δ -ketopentane- α - γ -tricarboxylate so formed, b. p. 198—200°/15 mm., is boiled with dilute hydrochloric acid. The δ -ketohectic acid is readily esterified by boiling with alcohol containing a little hydrogen chloride.

Ethyl δ -keto- α -methylhexoate, b. p. 110—112°/13 mm., and the

free acid, b. p. 157—159°/13 mm., are prepared by the interaction of a solution of ethyl sodioacetoacetate and ethyl methylacrylate, followed by boiling the *ethyl ε-ketohexane-βδ-dicarboxylate* so formed, b. p. 152—156°/12 mm., with hydrochloric acid.

Ethyl δ-keto-αα-dimethylhexoate, b. p. 110—115°/13 mm., is obtained from the acid, this being formed by heating methyl 4:6-diketo-2:2-dimethylcyclohexane-1-carboxylate (from mesityl oxide and methyl sodiomalonate) with barium hydroxide and water at 150° (compare Bredt, A., 1898, i, 264).

B. *Condensations of the δ-Ketonic Esters with Ethyl α-Bromo-isobutyrate*.—These condensations are brought about by means of zinc turnings, and the lactonic esters are isolated in the usual way. Ethyl δ-ketohexoate gives the lactone of δ-hydroxy-ε-carbethoxy-

δε-dimethylheptoic acid,
$$\text{CO}_2\text{Et} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{O} - \text{CO} - \text{CH}_2$$
 m. p.

176—177°. Ethyl δ-keto-α-methylhexoate yields the lactone of δ-hydroxy-ε-carbethoxy-αδε-trimethylheptoic acid, b. p. 169—171°/12 mm., and the third ester produces the lactone of δ-hydroxy-ε-carbethoxy-ααδε-tetramethylheptoic acid, b. p. 170—175°/12 mm.

C. *Hydrolysis of the δ-Lactonic Esters*.—The first two lactones are readily hydrolysed to the esters of unsaturated dicarboxylic acids by boiling them with alcoholic hydrogen bromide, but the third lactone has a very stable ring. βγ-Dimethyl-Δ¹-hexene-βζ-dicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{CMe}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$, from the first lactone, forms stout needles, m. p. 108—109°, gives an ethyl ester, b. p. 153—157°/12 mm., and yields acetic, isobutyric, and succinic acids on oxidation with permanganate. βγ-Dimethyl-Δ¹-heptene-βζ-dicarboxylic acid, from the second lactone, has m. p. 84—85°, and its ethyl ester has b. p. 153—157°/12 mm.

D. *Preparation of the Polymethylcyclohexenones*.—When the ester of the above hexenedicarboxylic acid is boiled with sodium powder in benzene, it yields a small quantity of ethyl 4-keto-2:3:3-trimethyl-Δ¹-cyclohexene-1-carboxylate, most of the material suffering complex condensation. This ester gives 2:3:3-trimethyl-Δ¹-cyclohexen-4-one on hydrolysis, b. p. 85—90°/12 mm.; semicarbazone, m. p. 168—171°. When methylated and then hydrolysed, it also forms 2:3:3:5-tetramethyl-Δ¹-cyclohexen-4-one, b. p. 90°/12 mm.; semicarbazone, m. p. 196—197°.

Displacement of the ethylene linking occurs if the unsaturated dicarboxylic acids are heated with acetic anhydride and then distilled. The hexenedicarboxylic acid yields 3:4:4-trimethyl-Δ¹-cyclohexen-5-one, b. p. 85—90°/14 mm., semicarbazone, m. p. 185—187°, which may be reduced by sodium and alcohol to 1:2:2-trimethylcyclohexan-3-ol, b. p. 85—87°/15 mm. The heptenedicarboxylic acid yields 3:4:4:6-tetramethyl-Δ¹-cyclohexen-5-one, b. p. 80—85°/13 mm.; semicarbazone, m. p. 178—179°.

J. C. W.

The Reduction of Aromatic Ketones. W. D. COHEN (*Rec. trav. Chim.*, 1919, 38, 113—131).—In continuation of previous

work (compare this vol., i, 124), the author has studied the reduction of a number of substituted benzophenones by aluminium amalgam in alcohol, and determined the proportions of substituted benzhydrol and benzopinacone formed in each case. The proportion of benzhydrol to benzopinacone is found to depend directly on the velocity with which the pinacone is decomposed in alkaline solution to give the hydrol and the ketone. Thus, then aluminium amalgam is, at the moment of reduction, a slightly alkaline reagent and promotes the secondary reaction, the products of which are dependent on the velocity with which the primary product, the pinacone, is attacked. The course of the reaction in the reduction of benzophenone consists of the preliminary formation of diphenylhydroxymethyl, $\text{CPh}_2\cdot\text{OH}$, which is immediately transformed into pinacone.

o-Chlorophenyl *p*-tolyl ketone, m. p. 99.5° , is obtained by the condensation of *o*-chlorobenzoyl chloride with toluene in the presence of aluminium chloride. It yields 2-chloro-4'-methylbenzhydrol, m. p. 67° , and 2-chloro-4'-methylbenzopinacone, m. p. $175\text{--}176^\circ$. *p*-Chlorophenyl *p*-tolyl ketone, m. p. 118° , similarly prepared, gives only the corresponding hydrol, m. p. 67.5° , by reduction in neutral solution, and the pinacone, m. p. 178° , by reduction in acid solution. W. G.

Some Ketone Condensation Reactions. SVEN BODFORSS (*Ber.*, 1919, 52, [B], 142—145).—The author has shown (A., 1917, i, 223; 1918, i, 229) that Widman's reaction (A., 1913, i, 1219; 1916, i, 406; 1917, i, 221) is not a general one for aldehydes. It is of interest, therefore, to ascertain what course the Erlenmeyer reaction will take when derivatives of chloroacetic acid other than the ethyl ester are employed. An alcoholic solution of benzaldehyde ($1\frac{1}{2}$ mols.) and chloroacetanilide cooled in a freezing mixture yields by treatment with sodium ethoxide solution and subsequent acidification with dilute acetic acid $\alpha\beta$ -oxido- β -phenylpropionanilide, $\begin{array}{c} \text{CHPh} \\ | \\ \text{O} \end{array} \text{---} \text{CH} \cdot \text{CO} \cdot \text{NHPh}$, colourless needles, m. p. 142° .

Phenyl $\alpha\beta$ -dichloro- β -*m*-nitrophenylethyl ketone, $\text{COPh} \cdot \text{CHCl} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, colourless crystals, m. p. 148° , is obtained by saturating a glacial acetic acid solution of ω -chloroacetophenone and *m*-nitrobenzaldehyde with hydrogen chloride in the cold, and also by leading chlorine into a solution of phenyl *m*-nitrostyryl ketone in the same solvent.

Cuminaldehyde and acetophenone, condensed by means of methyl-alcoholic sodium methoxide, yield phenyl isopropylstyryl ketone, $\text{C}_6\text{H}_4\text{Pr}^i \cdot \text{CH} \cdot \text{CH} \cdot \text{COPh}$, b. p. $225\text{--}227^\circ/15$ mm. (slight decomp.), which forms a dibromide, needles, m. p. $119\text{--}119.5^\circ$.

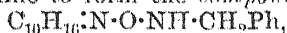
C. S.

Theory of Colour Lakes. Action of Potassium Ferri-cyanide on Alizarin in Alkaline Solution and the Constitution of Hydroxyanthraquinones. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 146—147).—A claim of priority over Scholl and Zinke

(this vol., i, 25. Compare also Baudisch, A., 1917, i, 356, 556; Baudisch and Klaus, *ibid.*, i, 331). C. S.

Optically Active Pinene Nitrosochloride, and Synthetic Active Pinene. E. V. LYNN (*J. Amer. Chem. Soc.*, 1919, **41**, 361—368).—In the preparation of the nitrosochloride from pinene by Wallach's method, it is well known that the yield of crystalline product varies inversely with the optical activity of the specimen, whilst the mother liquor remains blue for some time with the most active oils. An obvious suggestion, therefore, is that the active nitrosochlorides are more soluble than the inactive one, but Tilden offered another explanation of the poor yield (T., 1904, **85**, 759—764). By varying the conditions of the experiment, somewhat better yields may be obtained and the active nitrosochlorides actually isolated.

Equal volumes of pinene, ethyl nitrite, and alcohol are mixed and treated at -5° with the requisite amount of hydrogen chloride dissolved in alcohol. Crystals of inactive pinene nitrosochloride are removed after half an hour, and the mother liquor is then diluted with alcohol and left at -10° , when the active modification gradually separates. The dextro-variety was obtained in this instance from American turpentine, and the lævo-modification from Oregon or Canada balsams. Active pinene nitrosochloride crystallises in transparent or cotton-like needles, m. p. $81-81.5^{\circ}$, $[\alpha]_D \pm 322^{\circ}$, and is appreciably soluble in most organic media. It reacts with benzylamine to form the compound,



m. p. $144-145^{\circ}$, $[\alpha]_D \pm 92^{\circ}$ in acetone, and with piperidine to give a similar compound, crystallising in rosettes, m. p. 84° , $[\alpha]_D \pm 50^{\circ}$. With alcoholic alkali hydroxide, it reacts to form nitrosopinene, and with aniline to give aminoazobenzene and active pinene; b. p. $155-159^{\circ}$, $n_D 1.470$, $[\alpha]_D \pm 53.75^{\circ}$ in 4% alcoholic solution. This "regenerated" α -pinene gave an inactive hydrochloride, like the natural product.

The existence of active nitrosochlorides in the mother liquors does not by any means fully account for the poor yields. Even inactive pinene only gives about 50% of the theoretical yield. As the blue solution deposits its colourless crystals, a gas is evolved which Tilden suggested might be nitrous oxide. It is now conclusively proved to be nearly pure nitrogen, and its volume agrees closely with that of the nitrogen unaccounted for. The mother liquor has been briefly examined, and found to be a complex mixture. J. C. W.

Keto-cineole. GUIDO CUSMANO (*Gazzetta*, 1919, **49**, i, 26—38).—When heated with ethyl alcohol, α -terpineol nitrosochloride is converted in satisfactory yield into keto-cineole-oxime, and this with nitrous acid gives quantitatively the pernitroso-compound, from which the free ketone is obtained, also quantitatively, by treatment with concentrated aqueous ammonia (compare Cusmano and Tinari, A., 1912, i, 272).

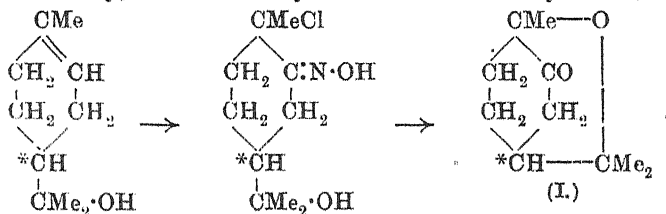
Saturated cyclic ketones containing ten carbon atoms in the molecule and possessing the $\cdot\text{CO}\cdot\text{CH}_2\cdot$ grouping and the general structure of keto-cineole may be divided into two groups: (1) menthone, tetrahydrocarvone, and tanacetone, and (2) camphor and pinocampnone. All show the same reactions of the carbonyl and of the adjacent methylene group, and opening of the fundamental hexamethylene nucleus between the carbonyl and the neighbouring tertiary (or quaternary) carbon atom is possible in all cases; rupture between the carbonyl and the methylene in addition is, however, possible only with the ketones of the second group. With the latter, which possess a "bridge," keto-cineole must be classed. Keto-cineole exhibits marked physiological activity, which is to be investigated.

Reduction of keto-cineole oxime by means of sodium and boiling amyl alcohol yields as one product an *aminocineole*, which forms a crystalline *platinichloride*, $(\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6\cdot 2\text{H}_2\text{O}$, m. p. 233° (decomp.).

Inactive keto-cineole forms shining, white, lamellar crystals, m. p. 42° , and yields a *semicarbazone*, m. p. 220° , and a *phenylhydrazone*, $\text{C}_{10}\text{H}_{16}\text{O}\cdot\text{N}_2\cdot\text{HPh}$, m. p. about 160° , which gradually loses phenylhydrazine.

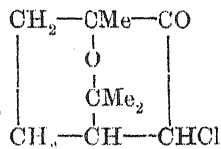
The use of inactive α -terpineol mixed with some of the dextro-rotatory form results in the formation of inactive and active keto-cineole-oximes. The active oxime forms prismatic crystals, m. p. 168° , $[\alpha]_D^{25}$ in methyl alcohol -11.8° . The active keto-cineole forms colourless, lamellar crystals, m. p. about 50° , $[\alpha]^{25} -44.0^\circ$.

Although keto-cineole contains two asymmetric carbon atoms, the optical activity, as is shown by the scheme of the synthesis,



is due only to the one marked with an asterisk, this being pre-existent in the active α -terpineol. T. H. P.

Halogenated Compounds of Keto-cineole. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 78—83. Compare preceding abstract).—Keto-cineole is readily converted into monochloro-(or monobromo-)keto-cineole (annexed formula), but further halogenation results in the formation of derivatives of carvomenthone (tetrahydrocarvone). The structure of the monohalogenated compounds is established by the action of potassium permanganate (three atoms of oxygen per molecule of halogen derivative) or of dilute potassium hydroxide solution, which



converts them into cineolic acid, this reaction being similar to the transformation of analogous camphor derivatives into camphoric acid. When treated with hydrogen bromide in ethereal solution, keto-cineole yields 1:8-dibromocarvomenthone (*loc. cit.*); the latter, and not 1:3:8-tribromocarvomenthone, is also obtained by the action of hydrogen bromide on monobromoketo-cineole under similar conditions, transformation of the cineole "bridge" being accompanied by elimination by reduction of the bromine atom from the methylene group next to the carbonyl.

Monochloroketo-cineole, $C_{10}H_{15}O_2Cl$, forms shining, elongated prisms, m. p. 78° , and volatilises unchanged (compare Cusmano, this vol., ii, 61).

Monobromoketo-cineole, $C_{10}H_{15}O_2Br$, forms transparent, colourless, prismatic crystals, m. p. about 90° , and when volatilised emits an odour of keto-cineole. By bromine (2 atoms per mol.) in chloroform solution, it is converted into a *compound*, which crystallises in nacreous, lamellar crystals, m. p. 143° , and appears to be a tetrabromotetrahydrocarvone, $C_{10}H_{14}OBr_4$. T. H. P.

Digitalis Glucosides. XXXIX. H. KILLIANI (*Ber.*, 1919, 52, [B], 200—205).—After many years of disappointment, the author has now succeeded in degrading a compound of the digitalis series, namely, digitogenic acid (A., 1902, i, 46), to simpler substances which may open up the way to a final elucidation of the composition of the glucosides.

When heated at 100° with ten times its volume of 50% alcohol and concentrated hydrochloric acid in the proportion 25:1, digitogenic acid is hydrolysed to a *lactone*, $C_8H_{12}O_2$ (this may be corrected in the future), m. p. 93° , $[\alpha]_D -79.5^\circ$, and a monobasic acid, $C_{20}H_{32}O_6$ (or $C_{20}H_{30}O_6$), which crystallises well from diluted acetic acid with $0.5H_2O$, has m. p. 112° , $[\alpha]_D -79.8^\circ$, and forms a *magnesium salt* with $6H_2O$. J. C. W.

Saponins. I. E. WINTERSTEIN and M. MAXIM (*Helv. Chim. Acta*, 1919, 2, 195—203).—A short summary of the present knowledge of saponins is given, and attention is directed to the need for more extensive studies of the sapogenins which remain when these glucosides are hydrolysed. For a preliminary investigation of this sort, the authors have chosen the saponins of the horse-chestnut and the soap-berry (*Sapindus saponaria*). These may be isolated as follows. The crushed or powdered material is extracted with ether, then with warm 95% alcohol in the presence of calcium carbonate, and the alcoholic extract is evaporated, diluted with water, and digested with lead hydroxide for several days. After filtering and removing lead from the filtrate, the solution is concentrated in a high vacuum. For the further purification of the saponins, dialysis may be advisable, as the plant material contains a good deal of sucrose.

Horse-chestnut saponin is readily hydrolysed by dilute acids in the cold. *Sapindus saponin*, however, is only partly degraded by

cold acids. It appears to be a mixture of glucosides, which gives a mixture of pentosides when partly hydrolysed ("initial sapogenins"), these being converted into the "end sapogenins" by means of warm acids. A pentoside is also formed when the saponin is left with dilute hydrogen peroxide at 40° for some days. The sugars present include *D*-fructose and *D*-glucose, and rhamnose and arabinose in the ratio 1:2 or 1:3, and the approximate composition of the saponin is roughly 33—35% "end sapogenin," 45% hexoses, and 15% pentoses.

Sapindus saponin may be brominated in methyl-alcoholic solution. The product has just the same foaming power as the original saponin, but is no longer hæmolytic; in fact, it hinders the hæmolytic activities of other saponins.

Only about 6 grams of pure sapogenin can be obtained from 100 grams of the crude saponin. The compound, $C_{18}H_{28}O_3$, has m. p. 319°, forms a mono-acetate, gives a fluorescent dye when condensed with resorcinol, and yields naphthalene derivatives on oxidation.

J. C. W.

Curcumin. PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 292—299).

Tannins. I. Hamameli-tannin. KARL FREUDENBERG (*Ber.*, 1919, 52, [B], 177—185).—Although the constitutions of Chinese and Turkish tannins have been elucidated in all essential points by the work of Fischer and his collaborators (1912—1918), the last remaining problems will evidently require time for their solution, because these naturally occurring amorphous substances are very probably inseparable mixtures of very nearly related polygalloyl-glucoses. Grüttner's hamameli-tannin is, however, a crystalline, and therefore probably individual, substance. With regard to its constitution, the only fact known is that it contains gallic acid and a new sugar (Fischer, A., 1913, i, 1352). Titration shows that there is no free carboxyl group. By treatment with diazomethane in acetone solution, hamameli-tannin yields a friable methyl derivative which yields gallic acid trimethyl ether by hydrolysis with *N*-sodium hydroxide. The prolonged treatment with 5% sulphuric acid required to hydrolyse the tannin also causes changes in the sugar produced. The author has therefore hydrolysed a dilute aqueous solution of the tannin covered with toluene with tannase (the preparation of which is described; dextrose must be removed), and obtained gallic acid and a sugar (calculated as a hexose) in quantities corresponding with the formula of a digalloyl-hexose.

The sugar, which has been obtained only as a yellow, viscous, lævorotatory syrup, has not been identified; it appears to contain a normal chain of six carbon atoms.

C. S.

Formation of Flavone or Coumarone Derivatives from Hydroxychalkones. J. TAMBOR and HANS GUBLER (*Helv. Chim. Acta*, 1919, 2, 101—111).—Tambor has recently developed an easy

method for the synthesis of hydroxyflavones, namely, by the action of alcoholic potassium hydroxide on the dibromides of acetoxychalkones (A., 1916, i, 831), and Oesterle and Kueny have used this process in showing the connexion between homoeriodictyol and luteolin (A., 1917, i, 703). It is now shown, however, that flavones are not always formed, coumarones or coumaranones resulting in some cases. Whether the five- or six-membered oxygen ring is formed seems to depend on the position of the substituents in the aldehyde component of the chalkone.

2':4':2-Trihydroxychalkone (2:4-dihydroxyphenyl 2-hydroxystyryl ketone) (Göschke and Tambor, A., 1912, i, 195) is converted into the *triacetate*, glistening needles, m. p. 170—171°, and the *dibromide* of this, which crystallises in long needles, m. p. 144°, is warmed with alcoholic potassium hydroxide, and thus condensed to 2':4'-dihydroxy-1-benzoylcoumarone, $C_6H_4 \begin{smallmatrix} O \cdot C \cdot CO \cdot C_6H_3(OH)_2 \\ | \\ CH \end{smallmatrix}$.

This crystallises as a woolly mass of yellow needles, m. p. 144°, forms a colourless *diacetate*, m. p. 119°, and may be synthesised by the condensation of resorcinol with coumarilic chloride in the presence of aluminium chloride.

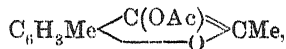
The methyl ethers of this coumarone are not easily obtained by direct methylation. They have been prepared by Rap's method for synthesising 1-benzoylcoumarones (A., 1896, i, 303), namely, by the interaction of salicylaldehyde and the mono- or di-methyl ethers of *o*-chlororesacetophenone (A., 1918, i, 395). 2'-Hydroxy-4'-methoxy-1-benzoylcoumarone forms small, lemon-yellow tablets, m. p. 253° (decomp.), and its *acetate* has m. p. 166°; 2':4'-dimethoxy-1-benzoylcoumarone forms colourless prisms, m. p. 102°. Other benzoylcoumarones prepared incidentally, in the same way, include 2'-hydroxy-4':6-dimethoxy-1-benzoylcoumarone, dark yellow tablets, m. p. 253° (decomp.) (*acetate*, m. p. 180°), from 2-hydroxy-3-methoxybenzaldehyde and *o*-chlororesacetophenone monomethyl ether, and 4'-hydroxy-6-methoxy-1-benzoylcoumarone, small, dull yellow prisms, m. p. 189°, from the same aldehyde and *o*-chloro-*p*-hydroxyacetophenone.

The influence of the position of the substituents is further illustrated by another example. 2-Acetoxyphenyl 4-methoxystyryl ketone dibromide yields *p*-methoxybenzylidenecoumaranone when treated with concentrated potassium hydroxide (Herstein and Kostanecki, A., 1899, i, 369), whereas 2-acetoxyphenyl 2-methoxystyryl ketone dibromide gives 2'-methoxyflavone. *o*-Hydroxyacetophenone and *o*-methoxybenzaldehyde are condensed by means of sodium hydroxide to 2-hydroxyphenyl 2-methoxystyryl ketone, yellow needles, m. p. 112°, the *acetate* of which, m. p. 64°, is converted into the *dibromide*, $OAc \cdot C_6H_4 \cdot CO \cdot CHBr \cdot CHBr \cdot C_6H_4 \cdot OMe$, m. p. 101° (decomp.), and then into 2'-methoxyflavone (2'-methoxy-2-phenyl- γ -benzopyrone), m. p. 103°, as indicated (compare A., 1912, i, 486). For comparison with *o*-methoxybenzylidenecoumaranone, this has been synthesised from coumaranone and *o*-methoxybenzaldehyde; it crystallises in straw-yellow prisms, m. p. 175°.

Other *benzylidene* coumaranones, prepared from suitable aldehydes and coumaranone, are as follows: 2-hydroxy-3-methoxy-, yellow needles, m. p. 212° (decomp.) (acetate, very pale yellow, silky needles, m. p. 176°); 2:3-dimethoxy-, long, pale yellow needles, m. p. 130°; 2:4-dimethoxy-, slender, bright yellow needles, m. p. 182—183°; 4-dimethylamino-, $\text{C}_6\text{H}_4 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}:\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, very dark red needles, m. p. 170—172°.

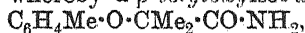
J. C. W.

Alkylated Coumaranones, especially 1:1:4-Trimethylcoumaranone. K. VON AUWERS and H. SCHÜTTE (*Ber.*, 1919, 52, [B], 77—92).—The production of *O*- and of *C*-alkyl derivatives of certain types of coumaranones has been already described (Auwers, A., 1912, i, 484, 486). The parent coumaranones have now been examined. 1:4-Dimethylcoumaranone, b. p. 138—140°/22 mm., which is best purified by distillation (A., 1915, i, 440), yields by acetylation 2-acetoxy-1:4-dimethylcoumaranone,



stout crystals, m. p. 29—30°, b. p. 170·5—171·5°/28 mm., which is converted into 1-chloro- and 1-bromo-1:4-dimethylcoumaranone, respectively, by chlorine or bromine in carbon disulphide solution, and easily undergoes fission by treatment with warm acids, being converted, therefore, by *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution into 4-hydroxy-*m*-tolyl methyl diketone di-*p*-nitrophenylhydrazone (A., 1918, i, 193).

1:4-Dimethylcoumaranone forms an *oxime*, $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$, colourless needles, m. p. 129°. The ketone, which yields chiefly the *O*-methyl derivative by shaking with methyl sulphate and sodium hydroxide solution (A., 1918, i, 27), is converted mainly into 1:1:4-trimethylcoumaranone by boiling with methyl iodide and sodium methoxide solution, or, better, by treatment with sodamide and methyl iodide in ethereal solution; in the former method about 20%, and in the latter about 5%, of the *O*-ether is produced. The *O*-ether is separated by conversion into the semicarbazone. The proof that the new methyl group is attached in position 1 is obtained indirectly by showing that 1:4-dimethylcoumaranone by ethylation and 4-methyl-1-ethylcoumaranone by methylation, as above, yield the same 1:4-dimethyl-1-ethylcoumaranone, b. p. 135—135·5°/18 mm., D_4^{20} 1·056, n_D^{20} 1·5359 (semicarbazone, colourless needles, m. p. 184—187°). A second proof is furnished by heating 1:1:4-trimethylcoumaranone with sodamide in boiling benzene or toluene, whereby α -*p*-tolylloxyisobutylamide,



colourless prisms, m. p. 84—85°, is obtained.

C. S.

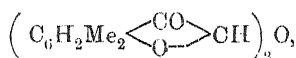
Coumaranones and Hydrindones. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1919, 52, [B], 92—113).—In connexion with the conversion of benzylidene derivatives of substituted

coumaranones into flavonols (Auwers and Pohl, A., 1914, i, 981) and the fission of the furan ring of coumaranones by semicarbazide and certain arylhydrazines (Auwers and Müller, A., 1918, i, 27), the evidence hitherto obtained has allowed certain generalisations to be made regarding the influence of substituents on the stability of the furan ring (Auwers and Müller, *loc. cit.*). To fortify this evidence, the behaviour of a further series of coumaranones towards semicarbazide and towards *p*-nitrophenylhydrazine has been examined. The coumaranone is treated with semicarbazide hydrochloride ($2\frac{1}{2}$ — $3\frac{1}{2}$ mols.) and sodium acetate in aqueous-alcoholic solution at 40°–50° for three to four days, or is heated on the water-bath for a few hours with *p*-nitrophenylhydrazine hydrochloride in aqueous-alcoholic solution; according as the product is a mono- or di-semicarbazone or a mono- or di-*p*-nitrophenylhydrazone, the furan ring of the coumaranone has not or has been ruptured. Thus 4-methoxycoumaranone yields the *semicarbazone*, $C_{10}H_{11}O_3N_3$, colourless needles, m. p. 225°–226°, 5-methoxycoumaranone yields the *semicarbazone*, $C_{10}H_{11}O_3N_3$, faintly yellow needles, m. p. 213°–215°, 3:5-dimethylcoumaranone yields the *semicarbazone*, $C_{11}H_{13}O_2N_3$, colourless needles, m. p. 249°–251°, and the *p*-nitrophenylhydrazone, $C_{16}H_{15}O_3N_3$, red needles, m. p. 233°, coumaranone yields *o*-hydroxyphenylglyoxaldi-*p*-nitrophenylhydrazone.

$OH \cdot C_6H_4 \cdot C(N \cdot NH \cdot C_6H_4 \cdot NO_2) \cdot CH \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2$, brownish-red, crystalline powder, m. p. about 265°, 5-methylcoumaranone yields 2-hydroxy-*p*-tolylglyoxaldi-*p*-nitrophenylhydrazone, m. p. about 260°, 6-methylcoumaranone yields 2-hydroxy-*m*-tolylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_5N_6$, brownish-violet, crystalline powder, m. p. about 270°, 5-methoxycoumaranone yields 2-hydroxy-4-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, $C_{21}H_{18}O_6N_6$, brownish-violet, crystalline powder, m. p. 264°, and 4-methoxycoumaranone yields 2-hydroxy-5-methoxyphenylglyoxaldi-*p*-nitrophenylhydrazone, reddish-brown, crystalline powder, m. p. 264°. 1:1:4-Trimethylcoumaranone (preceding abstract) yields a *p*-nitrophenylhydrazone, $C_{17}H_{17}O_3N_3$, canary-yellow needles, m. p. 148°. The results confirm the generalisations previously made, to which a fourth is now added, namely, the furan ring of 1:1-dialkylcoumaranones is characterised by its special stability.

Since it is possible that the varying stability of the coumaranones towards ketone reagents may be conditioned by their varying tendency to undergo enolisation, the behaviour of the substances during acetylation and during bromine titration by Meyer's method has been examined. No differences could be detected. All the coumaranones acetylate smoothly (of course, provided there is a hydrogen atom in position 1). Meyer's bromine method shows that the coumaranones in question (that is, coumaranones which do not contain an acyl substituent in position 1 [compare Auwers, A., 1912, i, 484, 1009]) are almost entirely ketonic in the solid state, in the fused state, and even after keeping in alcoholic solution for several days. 5-Methoxycoumaranone yields 2-acetoxy-5-

methoxycoumarone, colourless needles, m. p. 74—76°, by treatment with cold pyridine and acetyl chloride, and 3:5-dimethylcoumaranone yields 2-acetoxy-3:5-dimethylcoumarone, colourless needles, m. p. 65—66°, by boiling with acetyl chloride, and 1-bromo-3:5-dimethylcoumaranone, yellow needles, m. p. 105°, softening at 103°, by treatment with bromine in carbon disulphide solution; the bromo-derivative is converted by sodium carbonate in boiling aqueous acetone into the *ether*,



colourless needles, m. p. 210—212°.

Since α -hydrindones are allied to coumaranones in structure, it is not impossible that they also might be ruptured in the 5-ring by ketone reagents. However, the following hydrindones all react normally with semicarbazide and with *p*-nitrophenylhydrazine: 1-hydrindone yields a semicarbazone, and *p*-nitrophenylhydrazone, $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}_3$, brownish-red leaflets (from xylene) or orange, crystalline powder (from glacial acetic acid), m. p. 234—235°, 2-methyl-1-hydrindone yields a semicarbazone, colourless, crystalline powder, m. p. 200° with previous softening, and a *p*-nitrophenylhydrazone, brownish-red, microscopic crystals, m. p. 167—168°, 2-phenyl-1-hydrindone forms a semicarbazone, stout crystals, m. p. 211—212°, and a *p*-nitrophenylhydrazone, red crystals and yellow leaflets, both having m. p. 174°, and changeable the one into the other by crystallisation from suitable solvents, 3-phenyl-1-hydrindone forms a semicarbazone, colourless crystals, m. p. 223—225°, darkening at 218°, and a *p*-nitrophenylhydrazone, brick-red crystals, m. p. 220—221°, and 6-methoxy-2-methyl-1-hydrindone, b. p. 148°/10 mm., D_{16}^{20} 1.116, D_{16}^{25} 1.1188, n_D 1.55310, n_D 1.55884, n_D 1.57529 at 16.9°, prepared from β -*p*-methoxyphenyl- α -methylpropionyl chloride, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{COCl}$, b. p. 167°/23 mm. (the acid itself, $\text{C}_{11}\text{H}_{14}\text{O}_3$, colourless needles and prisms, m. p. 40°, b. p. 308°, is obtained from ethyl *p*-methoxy- α -methylcinnamate, b. p. 176—177°/15 mm., D_{16}^{20} 1.0894, D_{16}^{25} 1.085, n_D 1.56213, n_D 1.57009, n_D 1.59339 at 15.6°, which is itself obtained by warming Wallach's ethyl β -hydroxy- β -*p*-methoxyphenyl- α -methylpropionate with phosphoryl chloride), forms a semicarbazone, colourless, crystalline powder, m. p. 215—216°, and *p*-nitrophenylhydrazone, yellow needles, m. p. 163—164°.

Since the hydrindone last mentioned corresponds in structure with 4-methoxy-1-methylcoumaranone, which is most easily ruptured by semicarbazide, it is improbable that any member of the hydrindone series can be ruptured by ketone reagents. None of them exhibits the character of an enol; they cannot be acetylated and do not absorb bromine in the Meyer titration method. Only in one case has the 5-ring of a hydrindone given evidence of instability; 2-phenyl-1-hydrindone, after exposure to air for three months, yields β -deoxybenzoin- α -carboxylic acid by auto-oxidation (compare Salway and Kipping, T., 1909, 95, 116). C. S.

Spectrochemistry of Coumaranones and of Allied Bicyclic Ketones. K. VON AUWERS (*Ber.*, 1919, **52**, [B], 113—129).—It has been shown (preceding abstracts) that the coumaranones behave as desmotropic substances towards chemical reagents, but in the solid or fused state are almost entirely ketonic. The same conclusion is reached on spectrochemical evidence. For coumarones of the type

$R\text{--}\langle\overset{\text{CR}'}{\underset{\text{O}}{\text{C}}}\rangle\text{--CH}$, the mean values of the specific exaltations are $E\Sigma_a + 0.67$, $E\Sigma_D + 0.72$, $E\Sigma_\beta - \Sigma_a + 37\%$ and $E\Sigma_\gamma - \Sigma_a + 40\%$ (A., 1915, ii, 297), and for those of the type $R\text{--}\langle\overset{\text{CR}'}{\underset{\text{O}}{\text{C}}}\rangle\text{--CR}''$, $E\Sigma_a + 0.87$, $E\Sigma_D + 0.92$, $E\Sigma_\beta - \Sigma_a + 46\%$ and $E\Sigma_\gamma - \Sigma_a + 51\%$. In both cases R' may be alkyl or alkyloxy-groups. When the constants of the coumaranones are calculated on the assumption that these are hydroxycoumarones, the mean values are $E\Sigma_a + 0.74$, $E\Sigma_D + 0.83$, $E\Sigma_\beta - \Sigma_a + 70\%$ and $E\Sigma_\gamma - \Sigma_a + 82\%$. The exaltations of the refractions agree with those of the coumarones, but not those of the dispersions.

Coumaranones of the type $R\text{--}\langle\overset{\text{CO}}{\underset{\text{O}}{\text{C}}}\rangle\text{--CR}''R$ must be ketonic. The constants for such are $E\Sigma_a + 1.31$, $E\Sigma_D + 1.41$, $E\Sigma_\beta - \Sigma_a + 89\%$ and $E\Sigma_\gamma - \Sigma_a + 105\%$. The mean values of coumaranones which are capable of enolisation, calculated for the ketonic formula, are $E\Sigma_a + 1.37$, $E\Sigma_D + 1.48$, $E\Sigma_\beta - \Sigma_a + 86\%$ and $E\Sigma_\gamma - \Sigma_a + 97\%$, values which agree with those of the preceding coumaranones. The optical evidence shows, therefore, that all coumaranones as yet examined are ketonic and not enolic in structure. It is also shown spectrochemically that the so-called coumaranonecarboxylic ester is really the enol, 2-hydroxycoumarilic ester, a result which confirms the chemical evidence (A., 1912, i, 1009).

It has been shown (Auwers, A., 1918, ii, 343) that 1-hydrindones and 1-ketotetrahydronaphthalenes exhibit higher exaltations than the homologues of acetophenone structurally allied to them. A further example is presented by 6-methoxy-2-methyl-1-hydrindone (preceding abstract) when compared with 3-methoxyacetophenone. The same phenomenon is seen with heterocyclic ketones containing two ring systems, such as the coumaranones and the chromanones. However, when the carbonyl group in a bicyclic ketone is not attached to the aromatic nucleus, no conjugation occurs, and such substances should be optically normal. This is practically the case with 2-hydrindone and the lactone of *o*-hydroxyphenylacetic acid, for which the values $E\Sigma_a + 0.40$ and $+0.10$, $E\Sigma_D + 0.42$ and 0.11 , $E\Sigma_\beta - \Sigma_a + 14\%$ and $+13\%$, and $E\Sigma_\gamma - \Sigma_a -$ and $+14\%$ respectively are recorded.

C. S.

Guvacine. K. HESS and F. LEIBBRANDT (*Ber.*, 1919, **52**, [B], 206—212. Compare A., 1918, i, 401—403).—In the earlier paper, guvacine was said to be demethylated arecaine, and dihydro-guvacine to be identical with isonipecotinic acid. Freudenberg, on the other hand (*ibid.*), claimed that guvacine is demethylated arecaine, which would make dihydroguvacine identical with

nipecotinic acid. Hess now agrees with Freudenberg, and with Winterstein and Weinlagen (this vol., i, 171). The discrepancy was due to the properties of *isonipecotinic* acid and dihydroguvacine not being sufficiently well established, and to the fact that a specimen of supposed nipecotinic acid obtained from technical "*α*-picoline" proved, after all, to be *isonipecotinic* acid.

Guvacine is therefore 1:2:5:6-tetrahydropyridine-3-carboxylic acid, guvacoline is its methyl ester, arecaidine its 1-methyl derivative, and arecoline the methyl ester of this, whilst arecaine is to be cancelled.

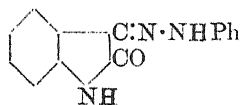
The statement in the earlier paper that methylguvacine gives the ethyl ester of guvacine when boiled with alcoholic hydrogen chloride is also in need of correction. The ester arose from unmethylated guvacine, and the ethyl ester of methylguvacine was left in the residue from the distillation.

The following table gives the corrected data for the decomposition temperatures of dihydroguvacine (from guvacine regenerated from guvacoline), nipecotinic acid (Ladenburg), and *isonipecotinic* acid, and their hydrochlorides, platinichlorides, and aurichlorides:

	Acid.	HCl.	Pt.	Au.
<i>iso</i> Nipecotinic acid...	328° (1H ₂ O)	280°	245°	213—214° (1H ₂ O)
Nipecotinic acid	249—250°	239—240°	212—213°	195—197°
Dihydroguvacine ...	252°	232—234°	235°	195°

J. C. W.

The Mobility of Hydrogen Atoms in Organic Molecules.
Action of Phenylhydrazine on Dioxindoles. J. MARTINET
 (*Compt. rend.*, 1919, **168**, 689—691).—Dioxindole and five of its



homologues, when acted on by phenylhydrazine, all gave phenylhydrazones of the type of the annexed formula, one molecule of the phenylhydrazine acting as an oxidising agent and the other combining to give the hydrazone.

Thus, in all these cases, a hydrogen atom attached to a carbon atom which was joined to a second carbon atom carrying a double linking was mobile.

W. G.

New Isomerism of the Isatogens. PAUL RUGGI (*Ber.*, 1919, **52**, [B], 1—8).—It is customary at present to represent isatogens by a quinonoid formula, $C_6H_4 \begin{smallmatrix} C(:O) \\ \diagup \quad \diagdown \\ N(:O) \end{smallmatrix} > CR$. By heating certain intensely coloured isatogens with alcoholic hydrogen chloride under pressure, the author has obtained less intensely coloured isomerides, for which there appears to be no formula possible except Baeyer's original formula for isatogens, namely, $O \begin{smallmatrix} N-C_6H_4 \\ \diagdown \quad \diagup \\ CR \cdot CO \end{smallmatrix}$. This formula accords well with the properties of the new isomerides. Thus 6-nitro-2-phenylisatogen, $NO_2 \cdot C_6H_3 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ NO \end{smallmatrix} > CPh$, is converted into

the *isomeride*, $\text{O} \begin{smallmatrix} \text{N} - \text{C}_6\text{H}_5 \cdot \text{NO}_2 \\ \text{CPh} \cdot \text{CO} \end{smallmatrix}$, pale yellow needles, m. p.

151—152°, which remains unchanged in pyridine solution after prolonged exposure to sunlight, forms an *oxime*, $\text{C}_{14}\text{H}_9\text{O}_4\text{N}_3$, yellow crystals, m. p. 180—181° (decomp.), and differs from 2:4-dinitrotolan in being saturated and in being precipitated unchanged by the addition of water to its solution in concentrated sulphuric acid.

Similarly, quinonoid ethyl 2-phenylisatogen-6-carboxylate is converted into an *isomeride*, faintly yellow needles, m. p. 100·5—101·5°, and methyl isatogenate is converted by methyl-alcoholic hydrogen chloride at the ordinary temperature into an *isomeride*, citron-yellow needles, m. p. about 165° (decomp., beginning at about 150°). The latter *isomeride* in acetone solution containing sodium iodide yields no iodine by acidification, whereas the corresponding quinonoid ester produces a considerable quantity by similar treatment.

C. S.

Amino-derivatives of *N*-Methylphenazthionium. F. KEHRMANN and PAULINE ZYBS (*Ber.*, 1919, **52**, [B], 130—141).—The two series of salts of *N*-methylphenazthionium correspond optically with those of phenazthionium, but are considerably less stable (Kehrmann and Sandoz, A., 1918, i, 126). Since it is known that the introduction of electropositive groups, such as alkyl and amino-groups, into the chromogens of "onium" dyes renders the salts more stable towards water, amino-derivatives of *N*-methylphenazthionium have been prepared. The salts, however, are less stable than was anticipated.

3-Nitro-*N*-methylthiodiphenylamine S-oxide,

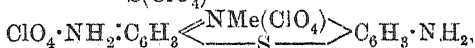
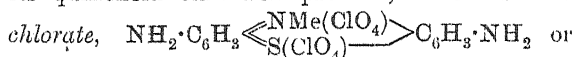


citron-yellow crystals, m. p. 177°, is obtained by the action of the strongest nitric acid in glacial acetic acid on *N*-methylthiodiphenylamine with cooling and the subsequent addition of water. By using twice the quantity of nitric acid, 3:6-dinitro-*N*-methylthiodiphenylamine S-oxide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NMe} \\ \text{SO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NO}_2$, is obtained,

pale yellow prisms, darkening at 280° and decomposing without melting at a higher temperature. The position of the nitro-groups in the *para*-positions to the nitrogen atom is proved by the identity of these nitro-derivatives with the products of the methylation of 3-nitro- and of 3:6-dinitro-thiodiphenylamine S-oxide (unpublished observations with Schmajewski). By reduction in alcoholic suspension with stannous chloride and hydrochloric acid, the mononitro-derivative yields the colourless stannichloride, and ultimately the *hydrochloride* of 3-amino-*N*-methylthiodiphenylamine, which is extremely unstable on account of its tendency to oxidise. By acetylation with sodium acetate and boiling acetic anhydride, the *hydrochloride* yields 3-acetylamino-*N*-methylthiodiphenylamine,

$\text{NHAc} \cdot \text{C}_6\text{H}_3 \langle \text{NMe} \rangle \text{S} \text{C}_6\text{H}_4$, colourless needles, m. p. 169° . The acetyl derivative in glacial acetic acid solution is converted by aqueous sodium nitrite into 3-acetylamino-N-methylthiodiphenylamine S-oxide, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \langle \text{NMe} \rangle \text{SO} \text{C}_6\text{H}_4$, colourless crystals, decomp. about 235° , and by concentrated aqueous ferric chloride into the ferrichloride, black needles, of the meriquinonoid dye, which is converted by perchloric acid solution into the perchlorate, $\text{C}_{30}\text{H}_{23}\text{O}_{10}\text{N}_4\text{Cl}_5\text{S}_2$, bluish-black needles. When 3-acetylamino-N-methylthiodiphenylamine is boiled with 50% sulphuric acid, a cherry-red solution of the meriquinonoid sulphate of the acetylated base is obtained. This becomes orange as the acetyl group is hydrolysed, and ultimately olive-green when the solution is treated with hydrogen peroxide and concentrated sulphuric acid. The olive-green colour of the di-acid salt of the holoquinonoid dye remains at first unchanged after diluting the solution with ice-water, but rapidly becomes dirty blue as the salt hydrolyses.

A similar series of compounds is obtained from 3:6-dinitro-N-methylthiodiphenylamine S-oxide, namely, 3:6-diamino-N-methylthiodiphenylamine dihydrochloride, unstable, colourless needles, and its quinonoid oxidation product, which is isolated as the diperchlorate,



violet leaflets with copper lustre (this salt is not hydrolysed by water), 3:6-diacetylamine-N-methylthiodiphenylamine, colourless needles, m. p. 265° , and 3:6-diacetylamine-N-methylthiodiphenylamine S-oxide, almost colourless crystals, decomp. about 270° .

C. S.

3:2'-Diquinolyl-2-carboxylic Acid. K. VON IHNATOWICZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 186—188).—2-Cyano-1-benzoyl-1:2-dihydro-3:2'-diquinolyl, $\text{CN} \cdot \text{C}_9\text{H}_6\text{BzN} \cdot \text{C}_9\text{H}_6\text{N}$, honey-yellow crystals, m. p. 210° , is obtained by adding benzoyl chloride to a suspension of 3:2'-diquinolyl in aqueous potassium cyanide solution (compare Reissert, A., 1905, i, 472, 925). When left with concentrated hydrochloric acid for twenty-four to forty-eight hours, it is hydrolysed, and, after neutralisation with sodium hydroxide, yields 3:2'-diquinolyl-3-carboxylic acid, $\text{C}_{19}\text{H}_{12}\text{O}_2\text{N}_2$, microscopic plates of rhombic habit, m. p. 192° (decomp.), which forms a silver salt, exhibits also basic properties, and is converted into 3:2'-diquinolyl by heating.

C. S.

Syntheses of 8:8'-Dihydroxy-5:5'-diquinolyl and a Case of Direct Chlorination by means of Ferric Chloride. L. T. BRATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 189—194).—When a solution of 8-hydroxyquinoline in about 3% hydrochloric acid is boiled with ferric chloride solution (80 grams in 200 grams of water) for two hours, and then basified with sodium hydroxide

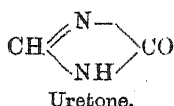
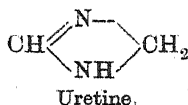
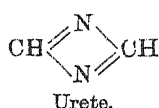
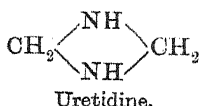
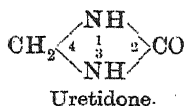
solution and the black precipitate boiled with concentrated aqueous sodium hydroxide, the alkaline solution contains as the chief product of the reaction 5:7-dichloro-8-hydroxyquinoline, the by-products being 5-chloro-8-hydroxyquinoline and the dihydroxy-diquinolyl described below.

When a 0.3% aqueous solution of 8-hydroxyquinoline at about 40° is treated with ferric chloride solution (35 grams in 100 grams of water), and is then treated as above, 8:8'-*dihydroxy-5:5'-diquinolyl* is obtained in considerable quantity, together with chlorinated products. The formation of the latter is avoided by using ferric sulphate in place of ferric chloride. The dihydroxy-diquinolyl, $C_{18}H_{12}O_2N_2$, forms brownish-yellow crystals, m. p. 320—322°, softening at 310°. It is soluble in dilute mineral acids and alkalis, forms a *hydrochloride*, $C_{18}H_{12}O_2N_2 \cdot 2HCl \cdot 2H_2O$, yellow crystals, and *diacetyl* derivative, crystals, m. p. 187°, softening at 180°, and has been prepared from 3:3'-diamino-4:4'-dihydroxydiphenyl by the Skraup reaction. C. S.

Four-membered Cyclic Ureas. I. History and Nomenclature. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1919, **41**, 370—378).—In 1869, Schiff obtained condensation products of urea with certain aldehydes, to which he assigned structures based on the ring system, $-N\langle C \rangle N-$. Since that time, Schiff's theory

has been practically abandoned (see, especially, Dixon's work on the formaldehyde reaction, T., 1918, **113**, 238), but other compounds have been discovered which unquestionably contain this heterocyclic system (see Fromm, A., 1893, i, 575; 1906, i, 656; 1913, i, 207; Frerichs and Hartwig, A., 1906, i, 74, 163; Senier and Shephard, T., 1909, **95**, 504).

In the further development of the subject which the author contemplates, a proper system of nomenclature for these four-membered ring compounds is desirable. Names with the root "diaz-" would be rational, but in recognition of Fromm's work as the pioneer, and of his terms "alduret" and "keturet," the following arrangement is adopted:



J. C. W.

Four-membered Cyclic Ureas. II. Condensation of IsoCyanic Acid with a Schiff Base. WILLIAM J. HALE and NORBERT A. LANGE (*J. Amer. Chem. Soc.*, 1919, **41**, 379—388).—When finely powdered potassium cyanate is stirred into a cold

concentrated solution of benzaldazine in glacial acetic acid and the solution is left in a vacuum desiccator over soda-lime for a few days at 0° , 1:4-diphenyluretidone, $\text{CHPh} \begin{smallmatrix} \text{NPh} \\ \text{NH} \end{smallmatrix} \text{CO}$, slowly separates in slender needles, m. p. $224\text{--}225^{\circ}$ (decomp.) (compare the result obtained by Bailey and Moore under other conditions, A., 1917, i, 355). The compound forms a 3-acetyl derivative, m. p. 237° , and yields benzaldehyde and phenylcarbamide on hydrolysis. It cannot, however, be obtained by the condensation of these two substances. If warmed together or mixed with a little alcohol and a few drops of sulphuric acid, they yield *benzylidenebisphenylcarbamide*, $\text{CHPh}(\text{NH}\cdot\text{CO}\cdot\text{NPh})_2$, m. p. $198\text{--}199^{\circ}$ (decomp.), whilst condensation with alcoholic hydrogen chloride furnishes the *hydrochloride of phenyl- α -ethoxybenzylcarbamide*, which is hydrolysed to the free base, $\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{OEt}$, an amorphous substance, softening at $150\text{--}155^{\circ}$, when its alcoholic solution is poured into water.

Benzylidene-ethylamine reacts with isocyanic acid in quite a different manner; no crystals separate, but if the acetic acid is removed by a current of steam, 4:6-diketophenyl-1-ethylhexahydro-1:3:5-triazine, $\text{CHPh} \begin{smallmatrix} \text{NEt}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} \text{NH}$, may be isolated in clusters of needles, m. p. 226° .

Staudinger has already directed attention to the similarity between carbimides and ketens with respect to their reactions with unsaturated compounds (A., 1917, i, 666), and it is noteworthy that he has found the same kind of divergence between benzylidene derivatives of aromatic and aliphatic amines as that illustrated above (A., 1910, i, 586).

J. C. W.

Diacetylintigotin. D. VORLÄNDER and JOHANNES VON PFEIFFER (*Ber.*, 1919, 52, [B], 325—329).—Proof is adduced that the acetyl groups in diacetylintigotin are attached to nitrogen, which helps to explain why the compound differs so widely from indigotin in colour.

Indoxylic acid, prepared by fusing the sodium salt of phenylglycine-*o*-carboxylic acid with sodium hydroxide, is heated with acetic anhydride at $90\text{--}100^{\circ}$, and thus converted into *N*-acetylindoxyl (A., 1901, i, 563). The position of the acetyl group follows from the fact that acetylanthranilic acid is formed if the compound is boiled with an excess of potassium permanganate in acetone. Diacetylintigotin is formed immediately, and it can be prepared conveniently in this way if an excess of permanganate is avoided. It crystallises from benzene in red prisms or pyramids, m. p. $245\text{--}250^{\circ}$, and yields a comparatively soluble form of indigotin when boiled with an acetic acid solution of hydrogen chloride.

O-Acetylindoxyl (*ibid.*) yields indirubin when oxidised by perhydrol in acetic acid solution.

Although indoxyl yields the two acetyl derivatives, indigo-white

only yields one diacetyl derivative. This is the *N*-isomeride, for it may be oxidised to acetylanthranilic acid.

Diacetyl-o-dimethylindigo-white, $C_{25}H_{20}O_4N_2$, obtained by acetylating the alkaline solution of "*o*-tolylindigo-white," crystallises in white tablets, m. p. 245—248°, and may be oxidised by nitrogen trioxide fumes to *diacetyl-o-dimethylindigotin*, orange-yellow tablets, m. p. 178° (decomp.). The corresponding *dibenzoyl* compound forms yellow crystals, m. p. 175° (decomp.). J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. IV. Chain Compounds of Sulphur (*continued*). PRAFULLA CHANDRA RAY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 261—271).

Dihydroxydihydroglyoxalines and their Conversion into Glyoxalines. II. OTTO DIELS and CARRY SALOMON (*Ber.*, 1919, 52, [B], 43—51. Compare Diels, A., 1918, i, 448).—Further experiments have been undertaken to characterise and to confirm the constitution of 3:4-oxido-2-phenyl-4:5-dimethyl-3:4-dihydroglyoxaline (*loc. cit.*). It reacts additively with acetyl chloride to form a compound, $C_{13}H_{15}O_2N_2Cl$, colourless crystals, m. p. 148°, with benzoyl chloride to form the compound, $C_{18}H_{17}O_2N_2Cl$, crystals, m. p. 162°, both of which are stable, with phenylcarbimide in pyridine solution to form the compound, $C_{18}H_{17}O_2N_3$, colourless crystals, m. p. 140°, and with ethylcarbimide in benzene solution to form the compound, $C_{14}H_{17}O_2N_3$, crystals, m. p. 116—118°. It is converted into 2-phenyl-4:5-dimethylglyoxaline by anhydrous ethylamine in benzene solution at 160°, or more smoothly by phenylhydrazine at 200—210°. C. S.

peri-Naphthylenediamine and Selenious Acid. O. HINSBERG (*Ber.*, 1919, 52, [B], 21—28).—The reaction studied by Sachs (A., 1909, i, 426) has been more thoroughly examined. *peri*-Naphthylenediamine (2 mols.) dissolved in pyridine is treated with a solution of selenious acid (1 mol.) in aqueous pyridine, whereby *dihydrodi-peri-naphthaselendiazole*, $C_{10}H_6 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{Se} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} C_{10}H_6$, is obtained after the addition of water. It forms yellowish-red flocks, m. p. 120°, and is oxidised very easily, even by air, to *di-peri-naphthaselendiazole*, $C_{10}H_6 \begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix} \text{Se} \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} C_{10}H_6$, brown, crystalline powder, m. p. above 300°, which is very sparingly soluble in all solvents except pyridine (*hydrochloride*, blackish-violet needles). *Di-peri-naphthaselendiazole* is decomposed by zinc dust, glacial acetic and concentrated hydrochloric acids on the water-bath, yielding hydrogen selenide and 1:8-naphthylenediamine, and is oxidised by ferric chloride and hydrochloric acid, yielding a black powder, decomp. above 300°, the nature of which has not been ascertained, but it is probably identical with the product obtained from equal molecular quantities of selenic acid and

1:8-naphthylenediamine by warming in dilute acetic acid solution on the water-bath.

The bearing of the preceding results on the author's theory of the structure of the selenium atom (A., 1918, ii, 106) is discussed.

C. S.

Distillation of Egg Albumin under Reduced Pressure.

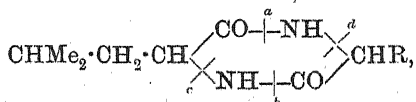
AMÉ PICTET and MARC CRAMER (*Helv. Chim. Acta*, 1919, 2, 188—195).—The tar obtained by the dry distillation of animal matter contains substances like aniline, pyridine, and quinoline which bear no relationship to the amino-acids of the proteins. The question arises, therefore, whether the protein complexes contain such atomic groupings, hitherto unrecognised, or whether these compounds are formed by the pyrogenic transformations or condensations of the primary decomposition products. In the hope of throwing some light on the problem, the authors have distilled 4 kilos. of egg-albumin under a pressure of 20—22 mm., but with little success.

Up to 70°, the only product is water; at about 150°, a brisk evolution of gas commences, mostly soluble in sodium hydroxide or dilute sulphuric acid; towards 220°, a yellow oil begins to distil, but at 350° distillation ceases, a very porous and light coke being left behind. The relative proportions of the products are as follows: water, 30%; organic compounds dissolved in this water, 6%; insoluble oil, 9%; coke, 32%; gas and losses, 23%.

The organic compounds are entirely soluble in ether, and can be differentiated into acidic, basic, and neutral fractions. Acetic, propionic, *n*-butyric, and succinic acids may be detected in the first fraction, but no aromatic acids. The bulk of the bases distils at about 175°, and appears to consist of a single primary *amine* of the formula C_6H_9N . It is a very mobile oil, which does not form a diazonium salt, but liberates benzene and nitrogen when warmed with nitrous acid. It is suggested, therefore, that the base may be a dihydroaniline of the formula $NH_2 \cdot CH < \begin{smallmatrix} CH_2 \cdot CH \\ CH=CH \end{smallmatrix} > CH$. It

forms a *picrate*, m. p. 185°, and may be acetylated or benzoyleated. Pyrrolic bases of higher boiling points are also present.

The chief product of the distillation is found among the neutral substances. It is *isohexoamide*, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$, m. p. 120°. The isolation of this amide has important consequences, since it throws light on the origin of the *isohexonitrile*, which is one of the principal constituents of animal oil (Weidel and Ciamician, A., 1880, 403), and also links this nitrile with leucine, the main product of hydrolytic cleavage, in a common stock, namely, a diketopiperazine ring substituted by an *isobutyl* radicle. Thus, in the formula



cleavage at *a* and *b* results in the formation of leucine, and at *c* and *d* in the production of *isohexoamide*. The neutral fraction contains other amides of fatty acids and compounds of the indole series, including indole itself, which has not been reported in animal oil.

It was expected that the aqueous portion of the distillate would contain *lævoglucosan* if egg-albumin contains a glucose grouping, but no trace of the substance could be detected. J. C. W.

Compressibility of Aqueous Solutions of Casein and Peptone. SVEN PALITZSCH (*J. Amer. Chem. Soc.*, 1919, **41**, 346—351, and *Compt. rend. Lab. Carlsberg*, 1919, **14**, 14—20).—The compressibility, hydrogen-ion concentration, viscosity, specific volume, and density of acid casein solutions, alkaline casein solutions, and peptone solutions have been measured for a series of concentrations at 20°. The compressibilities were measured over the range 100—300 megabars. The compressibility of casein solutions decreases with rising concentrations, and very nearly to the same extent in weakly acid and in weakly alkaline solutions. The compressibility of peptone solutions also decreases, even more markedly, with rising concentration. For the concentration of 10 grams in 100 grams of water, the compressibility of acid casein solution is 40.6×10^{-6} , of alkaline casein solution 40.5×10^{-6} , and of a peptone solution 39.0×10^{-6} . J. F. S.

Nuclein Metabolism. VI. The Cleavage of Nucleotides by means of Hot Aqueous Picric Acid Solutions. Isolation of Crystalline Cytidine-phosphoric Acid. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1919, **104**, 65—72).—The triphosphonucleic acid obtained from yeast-nucleic acid by hydrolysis with ammonia was further hydrolysed by treatment with hot picric acid solution. From the reaction mixture, a crystalline, brucine salt of cytidine-phosphoric acid was isolated,

$C_9H_{14}O_8N_3P(C_{23}H_{26}O_4N_2)_2$,
m. p. 180—182°. This yielded the free cytidine-phosphoric acid, $C_9H_{14}O_8N_3P$, in a crystalline condition, monoclinic-sphenoidal crystals, m. p. 227°, $[\alpha]_D^{20} = +23.43^\circ$. The two triphosphonucleic acids previously described (A., 1918, i, 47) were submitted to the picric acid hydrolysis. Both yielded the brucine salt of cytidine-phosphoric acid, but only from the *l*-triphosphonucleic acid, m. p. 205°, was the free cytidine-phosphoric acid isolated in the crystalline condition. The inactive triphosphonucleic acid, m. p. 185—187°, is therefore not regarded as a pure substance.

A mixture of uridine-phosphoric acid and cytidine-phosphoric acid may be obtained by hydrolysis of yeast-nucleic acid with picric acid, and the two products may be separated by careful fractional recrystallisation of their brucine salts. J. C. D.

Absorption of Water by Gelatin. EDITH B. SHREEVE (*J. Franklin Inst.*, 1919, **187**, 319—337).—The amount of water

absorbed by a gelatin jelly invariably increases with rise of temperature. Since the absorption is accompanied by development of heat, and contraction, Le Chatelier's theorem would require a decreasing water absorption for increasing temperature; it is suggested that the apparent discrepancy is due to the very slow rate of the reaction, equilibrium not being reached before decomposition of the gelatin begins. Hofmeister's results are confirmed, the amount of absorption in some salt and other solutions being less than in water, but greater in other solutions; if, however, the jellies are made up with these solutions instead of with water, the amount of water absorption is in all cases greater than for a jelly made with water only. The bearing of this result on biological conclusions drawn from imbibition experiments is discussed. [See also *J. Soc. Chem. Ind.*, 1919, 297A.] B. V. S.

The Influence of Saponin on the Action of Lipases. A. L. FLOHR (*Arch. Néerland. physiol.*, 1919, 3, 182—189).—Solutions of saponin activate pancreatic lipase, the influence exerted increasing with the concentration of the saponin up to 2% and then decreasing, using equal volumes of oil and saponin solution. The curves showing these results are analogous to those representing the variation of surface tension of saponin solutions with concentration.

On the other hand, saponin exerts an inhibiting action on the lipase of ricin, the influence increasing steadily with the concentration of the saponin. W. G.

Preparation of Primary and Secondary Arsanilic Acids. PHILIP ADOLPH KOBER and WALTER S. DAVIS (*J. Amer. Chem. Soc.*, 1919, 41, 451—458).—The preparation of the so-called primary arsanilic acid was first described by Béchamp in 1863, but the details of the processes which are in use on the large scale, are comparatively secret. The authors have now discovered a simple method for making either the primary or secondary arsanilic acid in a pure state (compare this vol., i, 182).

p-Aminophenylarsinic Acid.—1000 C.c. of technical arsenic acid (76%) are concentrated to 100% by heating at 120—140° for twelve to fifteen hours, then cooled, and stirred into 1400 c.c. of dry, ice-cold aniline. The arsenate so formed (aniline:acid, 3:2) is ground to a powder, and then 200 grams of it are stirred at 160° until molten, and finally heated under reflux for one to one and a-half hours at 160—170° and for one hour at 180—185°. After cooling somewhat, 225 c.c. of 6*N*-sodium hydroxide and 225 c.c. of water are added, when the unchanged aniline is run off and the aqueous layer is shaken with kaolin or kieselguhr, and filtered. The clear solution is mixed with 100 c.c. of 6*N*-hydrochloric acid, and then small portions are tested to see how much more acid is required to cause the complete precipitation of the arsanilic acid. When this has been added, the almost solid mass is filtered, washed by suspending it in 200 c.c. of water, and filtered again.

Di-p-aminophenylarsinic acid, $\text{OH}\cdot\text{AsO}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$.—56.4 C.c. of commercial arsenic acid and 1500 c.c. of aniline are heated at 230° in a flask fitted with an inlet tube reaching to the bottom and a condenser, a current of air being drawn through the liquid to ensure good mixing. When about 1200 c.c. of aniline have distilled over, the product is cooled, shaken with 3*N*-sodium hydroxide, and the aqueous layer is then agitated with infusorial earth and filtered. The solution is acidified by 3*N*-acetic acid, and the crude *sec*-arsanilic acid which separates is purified by dissolving in 3*N*-alkali, removing any aniline by a current of steam, and then adding acetic acid, first until a small precipitate of coloured products is formed, and finally until the acid is completely reprecipitated.
J. C. W.

Preparation of Sodium *p*-Hydroxyphenylarsinate. JAMES B. CONANT (*J. Amer. Chem. Soc.*, 1919, 41, 431—435).—The preparation of *p*-hydroxyphenylarsinic acid from phenol and arsenic acid represents a first stage in the synthesis of "salvarsan," but little has been published about the reaction beyond the notes of the German patent (A., 1909, i, 279). It is now stated that the best results, giving a yield of about 21.5%, are obtained by heating a well-stirred mixture of phenol and a syrupy arsenic acid corresponding with the formula H_3AsO_4 , at 147 — 157° , for three hours. An excess of acid is used amounting to 10% of the theoretical requirement, and practically nothing but a small quantity of water is lost during the process. The isolation of the sodium salt of the product is best performed as follows. The aqueous solution of the crude acid is filtered from tar, mixed with barium hydroxide until the brown colour begins to change to pink, and then extracted several times with ether to remove tarry matter. More barium hydroxide is then added until a test portion, after rendering it alkaline and filtering, shows the presence of barium ions, when the solution is made just alkaline by the addition of sodium hydroxide, and filtered. The excess of barium is removed by sodium sulphate, and the filtrate evaporated to a red syrup. Impurities are now finally removed by adding sulphuric acid until the colour becomes yellow, when they separate as a viscous, brown oil. The clear solution is then neutralised again and evaporated, a mixture of sodium sulphate and *p*-hydroxyphenylarsinate being obtained. If desired, the latter salt can be extracted by means of alcohol and crystallised.

The next step in the synthesis of "salvarsan" is the nitration of the *p*-hydroxyphenylarsinic acid. For this purpose, the above mixture of sodium salts is quite suitable, but it must be roughly analysed before use. This can be done by taking advantage of the fact that the arsinic acid is converted into tribromophenol on the addition of bromine water. In the nitration, the crude salt, dried at 100° , is stirred into about half its weight of sulphuric acid at 0° , and the nitrating mixture, containing one equivalent of nitric acid, is slowly added. The temperature is allowed to rise gradu-

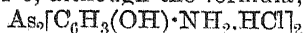
ally to 10°, when the mixture is diluted and the nitro-compound filtered next day.

J. C. W.

Arsenical Compounds. WALTER A. JACOBS, WADE H. BROWN, MICHAEL HEIDELBERGER, and LOUISE PEARCE (Amer. Pats. 1280119—1280223 and 1280225—1280227).—Several derivatives of *N*-phenylglycine-*p*-arsinic acid are described in which the aromatic nucleus containing the arsenic radicle is connected with the α -amino-group of an α -aminoacylamino-side-chain. These compounds are powerful agents in the treatment of trypanosomal and spirochætal infections. The general methods of preparation consist in treating the sodium salt of *p*-aminophenylarsinic acid with amides, ureides, or anilides of halogenacetic acids, or by treating the methyl ester of *N*-phenylglycine-*p*-arsinic acid with an amine. U.S. Pat. 1280119 relates to amides of *N*-phenylglycine-*p*-arsinic acid or substituted derivatives of the general formula $\text{—NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NR}'\text{R}''$, where R is alkyl, aryl, or hydrogen, and R' and R'' are alkyl or hydrogen. 1280120 relates to *N*-phenylglycine- β -methylureide-*p*-arsinic acid, or generally to derivatives having the side-chain $\text{—NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NR}'\text{H}$, in which R and R' are alkyl, aryl, or hydrogen. 1280122 relates to *m*'-amino-phenol-*N*-phenylglycine-*p*-arsinic acid, or generally to derivatives with the side-chain $\text{—NH}\cdot\text{CHR}\cdot\text{CO}\cdot\text{NHAr}$, in which R is alkyl, aryl, or hydrogen, and Ar is an aromatic radicle with or without substituted groups. 1280122 relates to arsenoxides containing the group —As=O , obtained by the action of mild reducing agents, such as sulphurous acid, on the amides and anilides specified above. 1280123 relates to arsenophenylglycinebisarylamides, obtained by the action of powerful reducing agents on the anilides specified above, whereby two molecules of the anilide unite together, by condensation and reduction, through the bond —As=As— . These are formed by the action of hypophosphorous and hydriodic acids on the corresponding arsinic acids or arsenoxides; they have a more powerful therapeutic effect than the arsinic acid derivatives. 1280125 relates to readily soluble sodium salts of the above ureides, 1280126 to readily soluble sodium salts of the above anilides, and 1280127 to readily soluble hydrochloric or other acid salts of the above arsenoaryl condensation derivatives, the salt-forming acid being attached to the α -amino-groups of the side-chains in the *para*-position to the arsenic.

J. F. B.

Preparation of Arsphenamine [Salvarsan]. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1919, **41**, 442—451. Compare this vol., i, 183).—The percentage of arsenic in salvarsan is generally found to be about 31·6, although the formula,



requires 34·2%. The difference is usually ascribed to the presence of two molecules of water, although the drug, as prepared by Ehrlich and Bertheim's method (*A.*, 1912, i, 523), is actually precipitated by methyl alcohol and ether, and these authors have shown that it contains one molecule of methyl alcohol. Kober is

of the opinion that the serious fluctuations in the toxicity of the various preparations, about 50% of which have to be rejected, are largely due to the use of methyl alcohol and ether, and has therefore designed a method for preparing the drug in which no use of these physiologically dangerous and inflammable solvents is made.

A solution of 85 grams of crude nitrohydroxyphenylarsinic acid in 290 c.c. of 2*N*-sodium hydroxide and 1700 c.c. of water is stirred into a solution of 220 grams of magnesium chloride and 1100 grams of sodium hyposulphite in 5500 c.c. of water. The mixture is kept at below 40° until the small amount of suspended impurities seems to be about to settle, when it is rapidly filtered, and the solution kept at 50—60° for two hours or so until the diaminodihydroxy-arsenobenzene is deposited. The yellow base is washed with ice-cold water, suspended in 400 c.c. of water, and dissolved in 2*N*-sodium hydroxide, 150 c.c. being sufficient as a rule, all the liquids being cooled to 0°. The solution is then filtered through an anærobic filter, mixed with 150 c.c. of hydrochloric acid (1:1), and then made up to 1700 c.c. The hydrochloride is finally "salted out" by slowly stirring the solution into 3250 c.c. of hydrochloric acid (1:1), and is dried in a vacuum desiccator over calcium chloride and sodium hydroxide.

Obtained in this way, salvarsan is a pale greyish-white powder containing 1 or 2H₂O, according to the drying, and charring at about 180°. It is less hygroscopic, and therefore more stable, than the ordinary preparations, and has a low grade of toxicity.

A summary of characteristic tests for salvarsan is given.

J. C. W.

Organo-chromium Compounds. F. HEIN (*Ber.*, 1919, 52, [B], 195—196).—By the action of magnesium phenyl bromide on anhydrous chromic chloride or chromyl chloride is obtained, together with other chromium phenyl compounds (as yet unexamined), an orange, amorphous substance which appears to be *chromium pentaphenyl bromide*, CrPh₅Br. It is not attacked by water, but is decomposed by acids, forms a *mercurichloride*, CrPh₅Br, HgCl₂, and has in boiling chloroform a molecular weight corresponding with its formula.

C. S.

Physiological Chemistry.

The Sugars of the Blood. J. W. BEST (*Arch. Néerland. physiol.*, 1919, 3, 222—266).—The blood of oxen and of horses, taken in the absence of digestion, contains 0.057—0.065% of dextrose, 0.002—0.005% of lactose, and <0.006—0.012% of an unknown sugar. Galactose, sucrose, melibiose, maltose, and isomaltose are

not present, or, if present, only in quantities less than 0.001%. The unknown sugar is formed by condensation from one or two molecules of a pentose, and contains about twelve atoms of carbon. It gives a phenylosazone, m. p. 181—182°, which from its crystalline form, solubility, and m. p. resembles the osazine of Cumming's sugar (compare *Proc. Roy. Soc.*, 1909, **81**, 374). The sugar is not attacked by either *Saccharomyces cerevisiae*, or emulsin, or the yeast which ferments lactose. It is dextrorotatory. It is not hydrolysed by boiling with dilute mineral acids, or at least only very slowly. The sugar exists as such in the blood, and is not formed during the hydrolysis of the gum of the blood.

The blood of human beings taken in the morning, eleven to sixteen hours after the last meal, contains 0.047—0.082% of dextrose, the residual reduction being equal to 0.019—0.031%, of which half is due to substances precipitable by phosphotungstic acid. Of the remainder, about 0.013% is due to the presence of the unknown sugar described above. Examination of the phenylosazones from the blood sugars before and after fermentation indicates the presence of lactose in human blood, and in one case, that of a woman, thirty-six weeks in pregnancy, 0.006% was found.

W. G.

Hæmocyanin. ERNST PHILIPPI (*Zeitsch. physiol. Chem.*, 1919, **104**, 88—94).—Hæmocyanin is very sensitive to acids. Snails' blood is immediately decolorised by the addition of small quantities of oxalic acid. After treating snails' blood with potassium hydroxide, a product was isolated which contained 7.0% of copper and gave an intense pyrrole reaction. The presence of manganese in the blood of *Pinna squamosa* is confirmed.

J. C. D.

The Effect of Acetone and of β -Hydroxybutyric and Acetoacetic Acids on the Blood Catalase. W. E. BURGE (*J. Biol. Chem.*, 1919, **37**, 343—347).—Introduction of doses of 5 grams per kilo. of 30% solutions of acetone, acetoacetic acid, and β -hydroxybutyric acid into the upper part of the intestines of rabbits produced a rise in the catalase content of blood taken from the jugular vein. Measurements of the catalase present in blood taken from the liver and the portal and jugular veins before and after the administration of these substances in this manner indicate that they stimulate the liver to an increased output of the enzyme. The increased oxidation in diabetes is attributed to the increased production of catalase resulting from such stimulation of the liver.

J. C. D.

The Mechanism of the Action of Fats in the Utilisation and Assimilation of Proteins. F. MAIGNON (*Compt. rend.*, 1919, **168**, 626—629. Compare A., 1918, i, 416).—The author reasserts his views as to the part played by the fatty acids in the building up of specific proteins in the body from the amino-acids arising from the ingested proteins (compare this vol., i, 185).

W. G.

Growth. XI. The Growth, and Senescence of White Mice fed upon Pituitary (Anterior Lobe) Tissue, Tethelin, Egg Lecithin or Cholesterol. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 393—426).—The results previously reported (A., 1916, i, 350, 690) dealt with the influence of these substances on the growth of mice up to the sixtieth week of life. The present paper records extended observations which cover the whole life-period of the animals. Generally speaking, the results confirm the conclusions announced in the earlier reports. The substances administered to the animals influenced the growth process in the way that catalysts influence chemical reactions, that is, by affecting the velocity with which the equilibrium is attained without affecting the equilibrium itself. J. C. D.

Growth. XII. The Influence of Pituitary Gland (Anterior Lobe) Tissue, Tethelin, Egg Lecithin, and Cholesterol on the Duration of Life of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 427—442).—The mean duration of life of mice which have received pituitary tissue, lecithin, or cholesterol lies within normal limits. Those which had received tethelin, the growth-accelerating substance isolated from the anterior lobe of the pituitary gland, showed a greatly extended duration of life. Male mice which had received tethelin continuously showed a duration of life which exceeded the normal by ninety-nine days, whilst in female mice which had received tethelin intermittently in three periods of one month each prior to the thirtieth week, the increased duration of life was eighty-one days. J. C. D.

Growth. XIV. Further Experiments on the Influence of Tethelin on the Growth of the White Mouse. T. BRAILSFORD ROBERTSON and L. A. RAY (*J. Biol. Chem.*, 1919, **37**, 455—463. Compare A., 1916, i, 356, 690).—Discontinuous administration of tethelin will produce the characteristic deformations of the growth curve of white mice. The same result was observed to follow a single relatively brief period of administration, namely, 4 mg. of tethelin per day for eight weeks only, from the fourth to the twelfth week of life. The concavity in the curve of growth is believed to be the expression of preliminary retardation preceding sexual maturity, followed by a secondary or compensatory acceleration accompanying and succeeding sexual maturity. The previous opinion, which held that both acceleration and retardation were directly due to tethelin, is now modified in that only the retardation is believed to be due to that substance, the acceleration being due to compensatory factors which develop in the animal itself in response to the abnormal dosage of the active principle of the anterior lobe of the pituitary body. The direct action of tethelin would thus appear to consist exclusively, so far as the whole animal is concerned, of retardation of growth. J. C. D.

Milk Coagulation and the Physical Condition of Milk Curd. O. ALLEMANN [with H. SCHMIDT] (*Kolloid Zeitsch.*, 1919, **24**, 27—42).—A number of experiments on the solidity of milk curds have been made in connexion with the manufacture of cheese. It is shown that the solidity of rennet curd is directly proportional to the time which has elapsed since coagulation, and inversely proportional to the time of coagulation. The solidity is proportional to the acidity of the mixture. The solidity of the milk curd is increased by the addition of potassium chloride in strict proportion to the amount of salt added. With increasing temperature, the solidity increases up to a maximum, but above 41—42° it decreases rapidly. The solidification of the curd is a continuation of the coagulation process, and it takes place according to the ordinary coagulation laws. The solidity is dependent on the individuality of the animal from which the milk was taken, and is constant over long periods of time. Sudden changes in the solidity relationships can occur; these are the result of weather changes and physiological conditions, and after a short time the solidity relationships return to their normal values.

J. F. S.

The Forms of Nitrogen in Protein-free Milk. CORNELIA KENNEDY (*J. Amer. Chem. Soc.*, 1919, **41**, 388—393).—The so-called protein-free milk is prepared as follows: 40 litres of centrifuged milk, diluted with 8 litres of water, are mixed with a little more than the required amount of hydrochloric acid to cause the formation of a curd, filtered through cheesecloth, the filtrate is boiled for half a minute, cooled, filtered through paper pulp, and the solution neutralised with sodium hydroxide and evaporated to dryness at 60—70°. An examination of the distribution of nitrogen in five samples of such milk, obtained from the same herd at different times, has been made, with the following results: (1) the nitrogenous substances present vary in composition; (2) considerable quantities of proteins or peptides of high molecular weight are still present, for there is a great increase in the amount of amino-nitrogen after hydrolysis or tryptic digestion; (3) nearly half of the nitrogenous material is precipitated by mercuric nitrate or phosphotungstic acid, the latter agent removing only non-amino-nitrogen.

J. C. W.

Action of 10 per cent. Thymol-Chloroform Preservative on the Chlorine Content of Urine. J. O. HALVERSON and J. A. SCHULZ (*J. Amer. Chem. Soc.*, 1919, **41**, 440—442).—A solution of thymol in chloroform is being widely used as a preservative for specimens of urine. Its influence on the content of inorganic chlorine has therefore been studied in the case of six alkaline specimens of cow's urine, stored at about freezing point for nearly two years, and sixteen specimens of acidic urine from swine, kept at the ordinary temperature for four to twenty-one days. No variations outside the limits of analytical errors were encountered.

J. C. W.

Cystine of Urine and of Urinary Calculi. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1919, 104, 129—132. Compare A., 1907, i, 476).—The cystine derived from the hydrolysis of hair and nails of a cystinuric patient was found to be identical with that present in the urine. Three cystine calculi contained traces of tyrosine, but a fourth was composed exclusively of cystine. This cystine possessed the same properties as that derived from the keratins.

J. C. D.

Hæmoquinic Acid. A New Disintegration Product of Quinine Present in the Urine, especially in "Blackwater" Fever. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 215—217).—Occasionally, dark-coloured urines have been observed to follow the administration of quinine. These cases were examined for the presence of kynurenic acid, but without success. An extension of the method for the isolation of kynurenic acid led, however, to the isolation of a new disintegration product of quinine, *hæmoquinic acid*. The acid crystallised from dilute alcohol has m. p. 183° (decomp.). It may be recognised in dilutions as great as 1 in 5000 by means of the blue coloration given with Herapath's reagent. It yields a *picrate*, m. p. 224°, and a *sulphate* crystallising from water in small, silky needles. In addition to "blackwater" urines, the urines of the following malaria cases were also examined for this acid: (1) patients having quinine; (2) patients soon after rigor; (3) patients some time after rigor. The results of this study suggest a possible relationship between the formation of hæmoquinic acid in the organism and the production of "blackwater." Hæmoquinic acid shows pronounced hæmolytic properties towards human and sheep's corpuscles. It is possible that the acid is 6-methoxyquinoline-3-glyoxylic acid, $C_9NH_5Me \cdot CO \cdot CO_2H$.

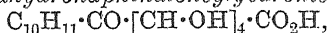
J. C. D.

Chitenine. A Disintegration Product of Quinine Found in the Urine. M. NIERENSTEIN (*J. Royal Army Med. Corps*, 1919, 218—219).—The observation of Kerner (*Arch. gesamt. Physiol.*, 1869, 200) that chitenine, an oxidation product of quinine, is found in the urine after the administration of quinine is confirmed. It is present in the urine in the early stages of the excretion of quinine. Chitenine was isolated from the urine of a normal individual collected during the first two or three hours after the administration of quinine sulphate by a fractionation of the precipitate produced on the addition of picric acid. The chitenine obtained from the urine crystallised from dilute alcohol in prisms, m. p. 281—282°, $[\alpha]_D^{25} -122.6^\circ$, and showed other properties similar to those of the chitenine described by Skraup (A., 1893, i, 737).

J. C. D.

The Fate of Tetrahydronaphthalene (Tetralin) in the Animal Body. JULIUS POHL and MARGARETE RAWICZ (*Zeitsch. physiol. Chem.*, 1919, 104, 95—104. Compare Schroeter and Thomas, A., 1918, i, 418).—Tetrahydronaphthalene is slightly

toxic, but rabbits weighing 2 kilos. can tolerate the administration of 2—3 grams by the stomach without showing apparent symptoms. Smaller animals develop diarrhœa and die, exhibiting narcosis. Tetrahydronaphthalene administered to the rabbit is excreted mainly as *ac-α-tetrahydronaphthaleneglycuronic acid*,



m. p. 256—258°, crystallising in colourless, lustrous plates. A small portion is excreted unchanged by the respiratory tract. When tetralin is administered orally to man, 5—7 grams per day, the urine is inactive, dark green, and readily yields an amorphous pigment. It also contains a leuco-compound, which is readily oxidised to a deep blue pigment, besides dihydronaphthalene and naphthalene. Dihydronaphthalene is chiefly excreted as the conjugated glycuronic acid, which readily yields naphthalene. Other substances isolated from the urines, such as *ac-α-tetrahydronaphthylcarbamide* and a substance melting at 286°, are regarded as products of secondary reactions. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Nitrate and Nitrite Assimilation. XIV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 35—40. Compare A., 1918, i, 474).—An explanation has now been found of the fact that iron as well as oxygen is necessary for the reduction. It has been shown (*loc. cit.*) that tervalent iron must be present in a complex form in order to produce nitric oxide or ammonia from an alkali nitrite. It is now shown that when an aqueous alkaline solution of sodium nitroprusside is boiled in the absence of air or oxygen, no nitric oxide is liberated, and that this gas is produced in large quantity directly oxygen is admitted to the system. A similar result is obtained by heating a solution of sodium carbonate and potassium nitrite with sodium ferripentacyanoammine, $[(\text{CN})_5\text{FeNH}_3]\text{Na}_3$, in the presence of oxygen. The whole process of the reduction of alkali nitrite is, therefore, a replacement of inorganic or organic groups co-ordinatively attached to the iron atom by the NO-group of the alkali nitrite, and the subsequent elimination of this group by oxygen on warming. In accordance with this, nitrous acid is found in the distillate when a solution of potassium ferrocyanide is boiled with sodium carbonate and sodium nitrite in the presence of oxygen. The elimination of the cyano-group, however, occurs only very slowly, so that only slight traces of nitric oxide are formed, but this gas is liberated in considerable quantity when a little pyridine is added to the reaction mixture. The pyridine may be replaced by phloroglucinol.

Contrary to previous statements, it is not necessary that the compound capable of entering into complex salt formation with the iron must be auto-oxidisable in order to reduce alkali nitrites in alkaline solution by heating.

The reduction of alkali nitrite to nitric oxide and ammonia by an alkaline solution of dextrose containing an iron salt is now comprehensible in view of the formation of the complex iron salts which are produced with aldo- and keto-hexoses in alkaline solution. Oxanthrone behaves quite similarly to dextrose, and in both cases oxygen is unnecessary. C. S.

Nitrate and Nitrite Assimilation. XV. Iron and Oxygen as Necessary Agents for the Reduction of Alkali Nitrates. OSKAR BAUDISCH (*Ber.*, 1919, 52, [B], 40—43. Compare preceding abstract).—Experiments are recorded which show that an alkali nitrate is quite unaffected by boiling in alkaline solution with ferrous carbonate or hydroxide in the absence of oxygen, but is reduced through the alkali nitrite to ammonia directly oxygen is admitted. Alkali nitrite is reduced to ammonia even in the absence of oxygen.

The author invokes his peroxide formula of alkali nitrates (A., 1916, i, 702) to explain the phenomenon. Probably the oxygen and the ferrous hydroxide form a compound, $\text{O} \begin{smallmatrix} \diagup \\ \text{O} \end{smallmatrix} \text{Fe}(\text{OH})_2$, and this and the alkali nitrate, reacting together like two peroxides, produce oxygen and alkali nitrite; the latter is then reduced to ammonia. C. S.

Influence of Salts on the Nitric-Nitrogen Accumulation in the Soil. J. E. GREAVES, E. G. CARTER, and H. C. GOLDTHORPE (*J. Agric. Res.*, 1919, 16, 107—135).—The object of the investigation was to determine the relative toxicity and stimulant action of various salts applied to a soil, as measured by the effect on the nitrifying organisms. The salts tested were the chlorides, nitrates, sulphates, and carbonates of sodium, potassium, calcium, magnesium, manganese, and iron. It was found that the toxicity of these salts was determined by the specific nature of the salt, and not by the ions. In order of decreasing toxicity, the salts were: sodium sulphate, sodium carbonate, calcium carbonate, potassium sulphate, potassium carbonate, ferric nitrate, sodium nitrate, magnesium sulphate, ferric sulphate, calcium nitrate, potassium nitrate, potassium chloride, magnesium nitrate, manganous carbonate, manganous chloride, manganous sulphate, ferric carbonate, magnesium chloride, sodium chloride, calcium chloride, calcium sulphate. Increase of toxicity with concentration was much more rapid in some cases than in others. The explanation of the toxicity is probably physiological, due to the action of the salt on the living protoplasm of the bacterial cell, the increased osmotic pressure of the soil solution being subsidiary.

Most of the salts acted as stimulants to nitrification in some at least of the concentrations used. Those which failed to give any stimulation were sodium sulphate and carbonate, calcium carbonate, potassium sulphate and carbonate, and ferric nitrate. Many of the nitrates caused large losses of nitric nitrogen, due to conversion into protein nitrogen, and not to denitrification. The fixation of nitrogen was specially stimulated by the nitrates of magnesium, iron, calcium, and manganese. [See *J. Soc. Chem. Ind.*, 1919, 297A.] J. H. J.

Preparation of Glycerol by Fermentation. KARL SCHWEIZER (*Helv. Chim. Acta*, 1919, 2, 167—172).—Glyceraldehyde and dihydroxyacetone are commonly regarded as intermediate compounds in the conversion of sugar into alcohol. It is possible, therefore, that they are also the precursors of the glycerol which is formed during alcoholic fermentation, in which case it might be possible to increase the yield of glycerol if the process is carried out in the presence of a reducing agent. Owing to the sensitive nature of the ferment, the problem resolves itself into finding a hardy species of yeast and a reducing agent which does not hinder its development. A technical pressed yeast, prepared with molasses, and sodium sulphite were found to answer the requirements. On the experimental scale, the best result was obtained in a Hayduck apparatus with a mixture containing 40 grams of sucrose, 2 grams of ammonium dihydrogen phosphate, 1 gram of dipotassium hydrogen phosphate, and 10 grams of pressed yeast in 400 c.c. of water, to which 30 grams of sodium sulphite were added when the fermentation had started. After twenty-four hours, fermentation had stopped, and as a mean of several experiments 21.3 grams of glycerol were obtained from 100 grams of sucrose. As might be expected, less glycerol was formed if the mixture was thoroughly aerated.

It is stated that some of the belligerent nations have applied sodium sulphite in the manufacture of glycerol by fermentation on the large scale during the war. J. C. W.

Fumaric Acid Fermentation of Sugar. FELIX EHRLICH (*Ber.*, 1919, 52, [B], 63—64).—The formation of free fumaric acid during the fermentation of sugar by *Aspergillus fumigatus* (Wehmer, this vol., i, 58) has been previously observed by the author during fermentation by *Rhizopus nigricans* (*Mucor stolonifer*) (A., 1912, ii, 192). C. S.

Determination of the Distribution of Nitrogen in Certain Seeds. J. F. BREWSTER and C. L. ALSBERG (*J. Biol. Chem.*, 1919, 37, 367—371).—Certain of the results have been reported previously (compare A., 1915, i, 760).—Yeast-nucleic acid, which was free from material giving a biuret reaction, was hydrolysed with 20% hydrochloric acid for twenty-five hours, and then analysed by the Van Slyke method for determining the distribution of

nitrogen in proteins. Fifteen % of the total nitrogen was found in the arginine fraction, although the nucleic acid contained no arginine. This indicates that in the determination of the distribution of nitrogen in materials containing nucleic acid by this method, erroneous results may be obtained, because purine and pyrimidine nitrogen may appear in the arginine fraction.

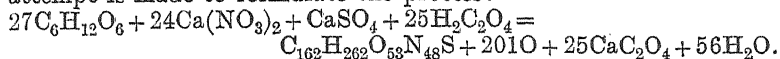
J. C. D.

The Influence of External Concentration on the Position of the Equilibrium Attained in the Intake of Salts by Plant Cells. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [B], 90, 448—470).—The authors have followed the course of intake of salts by carrot and potato tissue by measuring the changes in conductivity of the solution of a salt presented to the tissue, working with concentrations varying from $N/10$ to $N/5000$. Carrot tissue is much more suitable than potato tissue for work of this character, since the exosmosis from carrot into distilled water is slight, whilst that from potato is considerable. In the case of copper sulphate, exosmosis exceeds absorption at all concentrations, this being characteristic of toxic substances, and the initial rate of exosmosis increases with increase in concentration of the toxic solution. With aluminium sulphate, the curves showing the change in conductivity of the external solution were similar to those obtained with copper sulphate, although aluminium sulphate is not toxic. The authors suggest that this may be due to the absorption of the aluminium ion, its place being taken by hydrogen ions or some other ions, which results in an increase in the conductivity of the external solution.

Carrot tissue absorbs potassium, sodium, and calcium chlorides in all the concentrations examined, the absorption at first being approximately proportional to the external concentration. As the absorption progresses, however, it tends towards an equilibrium condition in which the ratio of internal to external concentration is not constant, but varies with the concentration. This ratio of final internal to final external concentration is called the absorption ratio, and may be expressed by the equation $y = kc^m$, where y is the final internal and c the final external concentration, k and m being constants. This is the adsorption equation, but the data given are regarded as inadequate to justify the conclusion that absorption of salts by the cell is an adsorption process. W. G.

Relationship between the Formation of Proteins and Acids in Leaves. ARTH. MEYER (*Ber. Deut. bot. Ges.*, 1918, 36, 508—513).—A review of the literature shows that slight protein formation accompanied by feeble deacidification and production of oxalate occurs in leaves kept in the dark; on exposure to light, the three processes occur to a greater extent. Protein and oxalate are readily formed in leaves exposed to light in an atmosphere free from carbon dioxide, and marked deacidification takes place simultaneously. The actions do not occur to more than a slight extent in the illuminated, colourless leaf.

The author is of the opinion that the carbohydrates react with nitrogen, sulphur, and phosphorus derived from inorganic salts to yield proteins; the bases of the salts are thereby liberated and neutralised by the organic acid produced in the leaves. An attempt is made to formulate the process:



Evidence in favour of such a scheme is deduced from the literature, and further quantitative data are promised.

H. W.

Utilisation of Dextrose and Lævulose by Higher Plants.

H. COLIN (*Compt. rend.*, 1919, 168, 697—699).—From an examination of etiolated leaves of beetroot, artichoke, and chicory fed by a root or a tubercle having a reserve of sucrose or inulin, the author produces further evidence in support of the view that lævulose is used by the cells more rapidly than is dextrose.

W. G.

Influence of certain Organic Compounds on the Development of Plants. III. G. CIAMICIAN and C. RAVENNA (*Atti Il. Accad. Lincei*, 1919, [v], 28, i, 13—20. Compare A., 1918, i, 473).

—The effect of watering bean plants grown on cotton wool with 0·1% solutions of various compounds related fundamentally to the vegetable alkaloids has been studied; the bases tested were applied in the form of tartrates or phosphates. Of the three methylamines, methylamine is the least toxic and the slowest, and trimethylamine the most toxic and the most rapid, in its action; small, yellowish-brown spots appear on the veins and then on the whole surface of the leaves, which finally dry up. The action exerted by tetramethyl- and tetraethyl-ammonium salts is less poisonous than, and different in its manifestation from, that of the amines. Theobromine and dimethylxanthine exert effects moderate in comparison with those of caffeine and trimethylxanthine. Methyluric acid has a distinctly toxic action, slow in appearing. Piperidine exerts a slight effect, but allows the plants to attain complete maturity, whereas 1-methylpiperidine, dimethylpiperidylammonium tartrate, coniine, acetyl piperidine, and piperine are all more or less toxic. Unlike morphine, codeine and diacetylmorphine are markedly toxic. Cinchonine exhibits the same poisonous effects as quinine, but to a less degree. Atropine and cocaine are both toxic, the action of the latter being the more prompt and more intense. Papaverine and narcotine are somewhat more toxic than morphine and produce similar effects, and sparteine also has a poisonous action. Strychnine at first causes increased development of the plants, but these die later; nicotine also kills the plants, but in 0·01% solution is without effect. *iso*-Amylamine rapidly produces fatal effects. Aniline is less poisonous than acetanilide, and this less so than methylacetanilide.

The above results indicate that introduction of methyl groups increases the toxicity of a compound, confirmation of this rule

being obtained with catechol and guaiacol. Potassium salicylate causes only retardation in development, whereas methyl salicylate exhibits distinct, although belated, toxicity.

Experiments with carbamide, guanidine, cyanamide, and potassium cyanate and cyanide show that cyanamide is the most poisonous of the first three compounds, and is followed by guanidine; carbamide, on the other hand, produces extraordinarily rank development of the plants. The cyanate and cyanide, both poisonous, determine retarded growth.

Some of the above poisonous compounds exert an influence on the migration of the starch, treatment of the leaves with iodine solution demonstrating the persistence of the starch at places where the action of light is excluded. The formation of starch also is sometimes retarded, coloration of the leaves by iodine exhibiting discontinuity in the form of spots and veinings.

T. H. P.

Microchemistry of Plants. XII. Large Siliceous Bodies in the Leaf of *Arundo Donax*. XIII. Behaviour of Cystolites towards Salts of Silver and other Metals. HANS MOLISCH (*Ber. deut. Bot. Ges.*, 1918, **36**, 474—481. Compare this vol., i, 113).—Unusually large siliceous bodies, 72—108 μ long, 43—100 μ wide at the ends, and 11—54 μ wide at the middle, occur in the leaves of *Arundo Donax*; they are insoluble in all acids except hydrofluoric, and can readily be examined after treatment of the leaf with phenol.

All the cystolites which have been investigated possess the power of reducing silver nitrate or sulphate so strongly that they become blackened after a short period. This property can be conveniently utilised for the investigation of the distribution of cystolites in leaves, the effects being well marked even with small magnification. The deposition of silver is due to calcium carbonate, which encrusts the cystolites; and the action provides a confirmatory microchemical method for the detection of calcium carbonate in the plant. Cystolites become coloured red to bluish-violet in gold chloride solution, rust-red in ferrous sulphate, pale green in nickel sulphate, and lilac or pink in cobalt chloride or cobalt sulphate. The colorations are due to precipitates of the corresponding hydroxides caused by the calcium carbonate of the cystolites.

H. W.

Production of Alcohol from Algæ. E. KAYSER (*Ann. Chim. anal.*, 1919, [ii], 1, 79—80).—See this vol., i, 193.

Carbohydrate Content of Lichens and the Influence of Chlorides on Alcoholic Fermentation. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 105—128).—Analyses of Iceland moss (*Lichen islandicus*) and reindeer moss (*Cladonia rangiferina*) are given. The former contains 59.45% of lichenin, 4.3% of fat, 4.73% of protein, 19.47% of organic matter, exclusive of lichenin, 2.01% of ash, and 10.04% of water. The latter contains 54.63% of lichenin, 2.59% of ether extract, 4.1% of protein, 26.96% of other organic sub-

stances, 10.59% of water, and 1.13% of ash. Hydrolysis of these two lichens with 2.5% hydrochloric acid or 6% sulphuric acid yields 60—66% of the dry weight of the raw material as dextrose. The sugar is fermentable. Sodium chloride disturbs the fermentation of dextrose according to the amount present. The concentration of dextrose also has an influence. A 12% solution of dextrose containing 4% of sodium chloride is completely fermented, and nearly so when 8% of the salt is present. Only 90% of the sugar is fermented when a 20% solution containing 4% of sodium chloride is tested. The equivalent quantity of calcium chloride exerts a more disturbing influence. The hydrolysates from the lichens contain not only the readily fermentable sugar, but also a substance which inhibits fermentation. It is possible this property belongs to the acids from the lichens. Lichens contain a readily hydrolysable cellulose. Lichenin is not converted into sugar by the disastatic ferments of the pancreas or saliva or plant diastases. Iceland moss contains at least 10.92% of lichen acids calculated as cetraric acid, $C_{30}H_{36}O_{12}$.
J. C. D.

Application of the Biochemical Method to the Study of Several Species of Indigenous Orchids. Discovery of a New Glucoside, Loroglossin. EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 701—703).—Using the method previously described (A., 1906, ii, 386), the authors have proved the presence in the aerial organ of a number of species of orchids of one or more glucosides hydrolysable by emulsin. From one of these orchids, *Loroglossum hircinum*, Rech., a new glucoside, *loroglossin*, has been isolated, having m. p. 137° (corr.), $[\alpha]_D -42.97^\circ$. It is hydrolysed by warm dilute sulphuric acid, as well as by emulsin. In addition, the plants contain sucrose and a considerable amount of a dextrorotatory substance, which is not attacked by ferments.
W. G.

The Flavones of Rhus. C. E. SANDS and H. H. BARTLETT (*Amer. J. Bot.*, 1918, **5**, 112—119; from *Physiol. Abstr.*, 1919, **3**, 578).—The wood flavone of *Rhus typhina* and *R. glabra* is fisetin, which is regarded as an end-product of metabolism. The distinctive leaf flavone of *R. glabra* and *R. copallina* is myricetin, which is probably a plastic substance. The authors agree with Perkin's views (T., 1896, **69**, 1299—1303, 1303—1309; 1898, **73**, 1016—1019; 1900, **77**, 423—432) that the flavones of the wood and of the leaves of *Rhus* are different.
W. G.

Chemical Investigations of some Poisonous Plants in the Natural Order Solanaceæ. III. Occurrence of Noryoscyamine in Solandra longiflora. J. M. PETRI (*Proc. Linn. Soc., N.S.W.*, 1917, **41**, 815—822; from *Physiol. Abstr.*, 1919, **3**, 581).—The leaves of *Solandra longiflora* contain alkaloids to the extent of 0.17% of the dry weight, the chief one being solandrine, and hyoscyamine is also present.
W. G.

Toxic Constituents in the Bark of *Robinia pseudacacia*, L. BUHACHIRO TASAKI and USHIO TANAKA (*J. Coll. Agric. Tokyo*, 1918, **3**, 337—356).—A new toxic glucoside, *robitin*, was isolated from the bark of *Robinia pseudacacia*. The air-dried bark was extracted with water; and the filtrate heated for half an hour at 80—90°, after which it was refiltered. The second filtrate was concentrated at 40° under reduced pressure to one-tenth of its volume. Impurities were separated by lead acetate, the excess of lead was then removed, and the process of concentration repeated. A reddish-brown extract was obtained, which was poured into absolute alcohol, when a white, flocculent precipitate was produced; this was washed with alcohol and dried in a vacuum. The yield was 3% of the dried bark. As thus prepared, robitin is a pure white, odourless, somewhat bitter, hygroscopic, amorphous powder, easily soluble in water and acids, but insoluble in organic solvents. It contained 3% of ash. On hydrolysis, it yielded glucose and rhamnose. [See *J. Soc. Chem. Ind.*, 1919, 267A.] J. H. J.

Copper and Zinc as Antagonistic Agents to the "Alkali" Salts in Soil. C. B. LIPMAN and W. F. GERICKE (*Amer. J. Bot.*, 1918, **5**, 151—170; from *Physiol. Abstr.*, 1919, **3**, 586).—Pot cultures of barley were grown on soils containing sodium chloride, sulphate, and carbonate in toxic quantities, to which copper in the form of its sulphate, chloride, or carbonate, or zinc in the form of its chloride or sulphate, was added. It was found that the presence of copper or zinc brought about an increased yield. W. G.

Presence of Acetylmethylcarbinol in Saccharine Sorghum Silage. W. G. FRIEDEMANN and C. T. DOWELL (*J. Ind. Eng. Chem.*, 1919, **11**, 129—130).—Saccharine sorghum silage is found to contain a volatile compound which reduces Fehling's solution and is identified as acetylmethylcarbinol; the latter was previously shown to exist in cider vinegar. The fact that acetylmethylcarbinol yields acetic acid on oxidation renders untrustworthy the Duclaux method for estimating alcohols, since, according to this method, the proportion of ethyl alcohol is calculated on the basis of the amount of acetic acid formed on oxidation. The saccharine sorghum silage is the only one in which formic acid has been found, this observation being probably connected with the fact that acetylmethylcarbinol yields formic acid as one of its products of oxidation. In none of the other silages examined could the presence of volatile reducing compounds be detected. T. H. P.

Organic Chemistry.

Organic Symbols. INGO W. D. HACKH (*Science*, 1918, 48, 333—335).—The author has evolved a "chemical shorthand" to represent the constitutional formulæ of organic compounds, for which is claimed the merits of compactness, exactness, accuracy, clearness, and simplicity. The atoms of the four elements carbon, hydrogen, oxygen, and nitrogen are to be imagined as points in the symbol, and these points are determined by lines (the bonds or valencies of the elements) terminating (hydrogen), meeting (oxygen and nitrogen), or crossing (carbon). Thus, a hydrogen atom is assumed to exist wherever a line ends, an oxygen atom wherever a line makes an angle or two lines meet, a nitrogen atom wherever three lines meet or arise, and a carbon atom wherever two lines cross or four lines radiate. Single bonds are represented by straight lines and double bonds by curved lines. The symbol for acetic acid is therefore $\text{—}\text{C}(=\text{O})\text{—OH}$. Numerous examples of symbols are given, including those for such complicated substances as morphine, hæmoporphyrin, and an octadecapeptide. An asymmetric carbon atom is indicated by a dot in the symbol. C. S.

The Atom of Bohr in Organic Chemistry. E. H. BUCHNER (*Chem. Weekblad*, 1919, 16, 521—527).—A theoretical paper in which the author applies the ideas of Rutherford and Bohr regarding atomic and molecular structure to organic compounds. As a consequence of the assumed mode of atomic linking, the symmetrical tetrahedral structure of the methane molecule is deduced, the replacement of one or more hydrogen atoms by substituents causing deformation of the regular tetrahedron. The theory is further applied to the elucidation of the nature of the double bond between carbon atoms. This is shown to differ from the single bond only in the greater radius of the electron orbit, in which four electrons are present instead of two, and in the consequent increased distance between the carbon nuclei. The geometrical isomerism of maleic and fumaric acids, and the transformation of *cis*- into *trans*-forms, are discussed. Kekulé's representation of the benzene molecule as a uniplanar hexagon of alternate singly and doubly linked carbon atoms receives support from the theory. The possible existence of two isomeric ortho-disubstitution products of benzene is admitted, but, owing to the essential qualitative similarity of the single and the double bond, already referred to, it is pointed out that the difference in properties of two such isomerides would probably be imperceptible. W. S. M.

A New Reaction of Paraffin Hydrocarbons. E. V. LYNN (*J. Amer. Chem. Soc.*, 1919, 41, 368—370).—When the reddish-brown solution of nitrosyl chloride in *n*-heptane is exposed to sun-

light, it gradually becomes blue and deposits ammonium chloride. The blue colour soon fades, and the turbid liquid then deposits a yellow oil, considerable volumes of hydrogen chloride being evolved. The oil decomposes further when submitted to steam distillation, hydroxylamine remaining in the residue. The distillate is very fragrant, and apparently consists of a mixture of the three *n*-heptanones, although no fraction yielded the semicarbazone of dipropyl ketone, m. p. 125°, which was made from calcium butyrate for comparison. Light petroleum exhibits the same phenomena.

In the case of heptane, it is assumed that the main reactions may be represented thus: $C_7H_{16} + NOCl = HCl + C_7H_{15}\cdot NO$ (blue), $C_7H_{15}\cdot ON \rightarrow C_7H_{14}\cdot N\cdot OH$ (oil), and this $+ H_2O = C_7H_{14}O + NH_3\cdot OH$. J. C. W.

Ethylene. WILLIAM MALISOFF and GUSTAV EGLOFF (*J. Physical Chem.*, 1919, 23, 65—138).—A résumé of the present state of knowledge of the physical and chemical properties of ethylene, and of the processes of its formation and decomposition. A very full bibliography is given. W. G.

The Action of Monosodioacetylene on some Halogen Esters of Secondary and Tertiary Alcohols. PICON (*Compt. rend.*, 1919, 168, 825—828).—The primary alkyl haloids react with monosodioacetylene in liquid ammonia to give homologues of acetylene (compare A., 1913, i, 438; 1914, i, 647). The secondary and tertiary alkyl haloids under similar conditions do not, however, give acetylenic hydrocarbons, but ethylenic hydrocarbons, a molecule of the hydrogen haloid being eliminated; thus:



W. G.

Action of Monosodioacetylene on some Iodides of Primary Alcohols with Branched Chains. PICON (*Compt. rend.*, 1919, 168, 894—896. Compare preceding abstract).—*iso*Butyl iodide when acted on by monosodioacetylene in liquid ammonia in an autoclave at the ordinary temperature is decomposed, giving *isobutylene*. Commercial *iso*amyl iodide, which is a mixture of the inactive and active forms, under similar conditions yields *isoeptinene* and β -methyl- Δ^2 -butene, together with a condensation product. The *isoeptinene* and the condensation product come entirely from the *i-iso*amyl iodide, whilst the *iso*amylene comes from the active isomeride.

Alkyl iodides of the type $R\cdot CH_2\cdot CH_2I$ yield true acetylenic hydrocarbons when decomposed by monosodioacetylene, whereas from iodides of the types $R\cdot CHR'\cdot CH_2I$ or $R\cdot CH_2\cdot CHR'I$ an ethylenic hydrocarbon is always formed. This formation of an ethylenic hydrocarbon is shown not to be due to the presence of traces of water or to any action of the liquid ammonia on the alkyl iodide. W. G.

Action of Magnesium Phenyl Bromide on Polyhalogenated Derivatives of Ethane. FRED. SWARTS (*Bull. Soc. chim.*, 1919, [iv], 25, 145—174).—In an endeavour to prepare difluorobromoethylbenzene by the action of magnesium phenyl bromide on $\alpha\alpha$ -difluoro- $\alpha\beta$ -dibromoethane, the author could only obtain difluoroethylene. He then studied this reaction with a number of other polyhalogenated derivatives of ethane, using, in every case, one molecule of the organomagnesium compound and one molecule of the substituted ethane. The reaction was, in every case, complex and gave rise to several different compounds. In the case of the bromo-derivatives of ethane, the principal reaction consisted in the elimination of two halogen atoms and the formation of an ethylene derivative and bromobenzene. When the halogenated ethane had an atom of fluorine and an atom of bromine attached to the same carbon atom, it was always the atom of bromine which was eliminated. In the case of a compound of the type $\text{CH}_2\text{I}\cdot\text{CHF}_2$, where an atom of fluorine and an atom of iodine were eliminated, the principal reaction always proceeded according to the equation $\text{CH}_2\text{I}\cdot\text{CHF}_2 + \text{MgPhBr} = \text{CH}_2\cdot\text{CHF} + \text{PhI} + \text{MgBrF}$. The chloro-derivatives behaved differently from the fluoro-, bromo-, or iodo-derivatives of ethane in that, instead of two halogen atoms being eliminated, a molecule of hydrogen haloid was eliminated. Thus tetrachloroethane yielded trichloroethylene and $\beta\beta$ -difluoro- $\alpha\alpha$ -dichloroethane yielded fluorodichloroethylene.

In several of the reactions where magnesium fluoride was formed, this salt was obtained in the form of a colloidal solution in water, the salt not being immediately precipitated by the addition of acid, and in certain cases the magnesium fluoride remained dissolved in ether.

In addition to the above general reaction, a number of secondary actions occurred, of which the most constant was the formation of diphenyl. The formation of this compound is most marked where the general reaction is slow, and less noticeable when the reaction is violent.

W. G.

Action of Alkaline Reducing Agents on Iodoform. A. GUTMANN (*Ber.*, 1919, 52, [B], 212—215).—When iodoform is added to a solution of arsenious oxide in about 27% sodium hydroxide, reaction takes place almost quantitatively, according to the equation $\text{CHI}_3 + \text{Na}_3\text{AsO}_3 + \text{NaOH} = \text{CH}_2\text{I}_2 + \text{NaI} + \text{Na}_3\text{AsO}_4$. Iodoform also oxidises sodium antimonite and stannite, and an alcoholic solution liberates sulphur from fresh sodium sulphide. When warmed with a mixture of sodium sulphide and cyanide, it produces a thiocyanate, but it will not oxidise a sulphite. J. C. W.

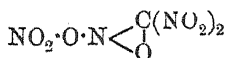
Preparation of Tetranitromethane. KENNEDY JOSEPH PREVITÉ ORTON (*Brit. Pat.*, 125000).—Acetylene is passed into nitric acid of 90—97.5% strength, preferably at a temperature of about 40°; absorption occurs more readily in the presence of mercury or a mercury salt, whereby also the yield is improved

when the operation is performed at 40°, but not at lower temperatures. The product is now mixed with sulphuric or fuming sulphuric acid under conditions excluding rise in temperature, and the mixture is gradually heated until the tetranitromethane distils, or slowly heated in a reflux apparatus until gas ceases to be evolved and then distilled. Apparently, the chief product of the action of acetylene on nitric acid is an intermediate compound, which is converted into tetranitromethane when the solution is heated with sulphuric acid. [See also *J. Soc. Chem. Ind.*, 1919, June.]

H. W.

Constitution of Tetranitromethane. ERICH SCHMIDT (*Ber.*, 1919, 52, [B], 400—413).—From the results of a quantitative study of the behaviour of tetranitromethane towards aqueous potassium hydroxide, it appears that the substance is decomposed in two ways, according to the equations: (1) $\text{C}(\text{NO}_2)_4 + 2\text{KOH} = \text{KNO}_3 + \text{KC}(\text{NO}_2)_3 + \text{H}_2\text{O}$ (compare Hantzsch and Rinkenberger, *A.*, 1899, i, 404), and (2) $\text{C}(\text{NO}_2)_4 + 6\text{KOH} = 4\text{KNO}_3 + \text{K}_2\text{CO}_3 + 3\text{H}_2\text{O}$. The course of the reaction depends on the concentration of the alkali; the ratio of the quantity reacting according to the first equation to that according to the second varies from 2:1 with 0.1*N*-alkali to 12:1 with 14*N*-alkali.

Iodotrininitromethane only reacts in one direction, however, analogous to (1) above: $3\text{CI}(\text{NO}_2)_3 + 6\text{KOH} = 3\text{KC}(\text{NO}_2)_3 + 2\text{KI} + \text{KIO}_3 + 3\text{H}_2\text{O}$ (Hantzsch, *A.*, 1906, i, 617). The dual nature of tetranitromethane is therefore connected with the fourth "nitro"-group, and the facts can be explained on the assumption that the compound exists in the tautomeric forms



(Willstätter and Hottenroth, *A.*, 1904, i, 472) and $\text{NO} \cdot \text{O} \cdot \text{C}(\text{NO}_2)_3$. The first form reacts according to equation (1), and is favoured by concentrated alkalis, whilst the second isomeride reacts according to equation (2).

In the quantitative study of the reaction, the following estimations were made: (1) The alkali required in the case of the 0.1*N*-solution. Sealed bulbs of the nitro-compound were crushed under the potassium hydroxide, and the excess of alkali was titrated, using phenolphthalein. (2) The nitrite. Immediately after the reaction with the alkali was completed, the clear solution was neutralised in the cold, and the nitrite estimated as nitrogen by means of ammonium chloride. (3) The carbonate. Some reactions were performed with 0.1*N*-barium hydroxide, and the barium carbonate produced was converted into the sulphate and weighed. (4) The nitrate. The product of the reaction with 0.1*N*-alkali was mixed with palladinised barium sulphate and concentrated potassium hydroxide, and treated with hydrogen until the solution became pale yellow. The nitroform was thereby reduced to an unknown compound, but the nitrate left almost untouched. The

filtered solution was then evaporated, dropped on hydrazine sulphate to decompose the nitrite, diluted, filtered again, acidified with sulphuric acid, and precipitated with nitron acetate. (The preparation of palladinised barium sulphate is described.) (5) The nitroform. The nitrite was decomposed by boiling with ammonium chloride, and then the solution was transferred to a flask with a ground-in still-head, acidified with phosphoric acid, and boiled until the nitroform had passed over, this being trapped in 0.1*N*-potassium hydroxide. The solution was acidified with acetic acid and precipitated with nitron acetate.

Tetranitromethane also decomposes into a nitrite when treated with dilute hydrochloric acid, for dimethyl-*m*-toluidine can be converted into its *p*-nitroso-compound by such a mixture.

The following salts of nitroform have been prepared: the stable *nitron* salt, $C_{20}H_{16}N_4, CH(NO_2)_3$, decomp. 136–141°; *di-isobutylamine* salt, decomp. 121–123°; *piperidine* salt, notched leaflets, decomp. 100°; *dibenzylamine* salt, needles, decomp. 160–163°.

J. C. W.

Preparation of Optically Active Propylene Glycol. AD. GRÜN (*Ber.*, 1919, 52, [B], 260–263).—Abderhalden has recently isolated the active forms of propylene glycol (this vol., i, 2), but Grün had already studied the subject with the partial success now described.

Propylene glycol is left with concentrated sulphuric acid at the ordinary temperature, and the inactive *dihydrogen disulphate*, $C_3H_6(O \cdot SO_3H)_2$, is isolated as the *barium* salt, $3H_2O$, which is converted into the *potassium* salt. leaflets, 0.5EtOH, *sodium* salt, needles, and *strychnine* salt. Two modifications of the last salt are obtained: pearly tablets, $[\alpha]_D^{20} - 20.38^\circ$, of which 0.9 gram dissolves in 100 c.c. of water, and rosettes of long, slender needles, $[\alpha]_D^{20} - 28.19^\circ$, with the solubility 11.82. By treatment with 0.2*N*-barium hydroxide, the tablets have been converted into the *barium* salt of *d*-propylene *dihydrogen disulphate*, $[\alpha]_D^{20} + 11.50^\circ$, but further progress in the isolation of *d*-propylene glycol could not be made, owing to the great stability of the free acid ester.

J. C. W.

Some Derivatives of Trimethylene Glycol. ERICH SCHMIDT and RUDOLF WILKENDORF (*Ber.*, 1919, 52, [B], 389–399).—Henry found in 1895 that “nitroisobutylglycerol,” $NO_2 \cdot C(CH_2OH)_3$, could be obtained readily by the condensation of nitromethane with formaldehyde under the influence of alkali hydroxides, but all his attempts at controlling the reaction so as to give nitrotrimethylene glycol were unsuccessful. The present authors have also found that partial condensation is hopeless, but have succeeded in making the glycol by the action of sodium methoxide solution on the glycerol, one molecule of formaldehyde being eliminated.

Nitroisobutylglycerol [nitrotrihydroxymethylmethane] is produced in 79% yield by warming a solution of nitromethane and

paraformaldehyde in dry ethyl acetate with a few drops of 33% potassium hydroxide. This is an improvement on Henry's method (A., 1896, i, 4). The *tribenzoate*, $\text{NO}_2 \cdot \text{C}(\text{CH}_2 \cdot \text{OBz})_3$, obtained by the action of benzoyl chloride and quinoline, crystallises in needles, m. p. 111° . The trihydric alcohol may also be prepared in methylalcoholic solution, and if such a solution is chilled and slowly mixed with sodium methoxide solution, *sodionitrotrimethylene glycol*, $\text{NO}_2 \cdot \text{CNa}(\text{CH}_2 \cdot \text{OH})_3$, separates in small prisms with 2MeOH , which crystallise with $2\text{H}_2\text{O}$ from aqueous alcohol, the yield being 91%. The salt decomposes vigorously at 130 – 136° , and gives the red colour with ferric chloride and the blue with ethereal hydrogen chloride, characteristic of the salts of nitro-paraffins. The salt is converted into free *nitrotrimethylene glycol* by boiling with ethereal salicylic acid. The compound crystallises from a mixture of ethyl acetate and chloroform in groups of feathery needles, m. p. 56 – 58° , is soluble in oxygenated solvents, does not give a colour with ferric chloride, is neutral to litmus, reduces ammoniacal silver oxide, decomposes when treated with benzoyl chloride and quinoline, and condenses with formaldehyde to give the above nitroisobutylglycerol.

If the sodium salt is treated with ethereal bromine, it gives a 97% yield of *bromonitrotrimethylene glycol*, which crystallises in groups of stout prisms, m. p. 120 – 122° , and forms a *dibenzoate*, $\text{NO}_2 \cdot \text{CBr}(\text{CH}_2 \cdot \text{OBz})_3$, in highly refractive prisms, m. p. 104° .

The nitro-compound is reduced by means of hydrogen, catalysed by palladinised barium sulphate, in oxalic acid solution. *Amino-trimethylene glycol* is a strongly alkaline syrup with a bitter taste, and forms a snow-white *oxalate*, decomp. 202° . When benzoylated by the Schotten-Baumann method, it yields the *N-benzoyl* derivative, which crystallises in delicate needles, m. p. 131° , with a bitter taste, whereas in the presence of quinoline the *tribenzoyl* derivative, $\text{NHBz} \cdot \text{CH}(\text{CH}_2 \cdot \text{OBz})_3$, is formed. This crystallises in needles, m. p. 136° , which no longer taste bitter. J. C. W.

Dichloroethyl Sulphide (Mustard Gas). III. Solubility and Hydrolysis of Dichloroethyl Sulphide with a New Method for Estimating Small Amounts of the Same.

E. F. HOPKINS (*J. Pharm. Expt. Ther.*, 1919, 12, 393–403).—The solubility of dichloroethyl sulphide in water has been determined, and at 10° has been found to be approximately 0.07%. The velocity of hydrolysis of dichloroethyl sulphide has been measured at 0.6° , 10° , 20° , 30° , and 37.5° ; the data are graphically represented in a series of curves. The hydrolysis is found to follow the equation for a unimolecular reaction.

Dichloroethyl sulphide in admixture with air may be rapidly estimated by bubbling the gas through a series of two tubes containing water at 35° ; the gas is rapidly absorbed and hydrolysed, and the hydrogen-ion concentration of the solution is then measured, methyl-red being used as indicator. It is necessary that all the glassware used should be insoluble in water. H. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VI. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RAY (T., 1919, 114, 548—552).

Preparation and Hydrolysis of Esters Derived from the Substituted Aliphatic Alcohols. GEORGE R. BANCROFT (*J. Amer. Chem. Soc.*, 1919, 41, 424—431. Compare A., 1918, i, 2).—A study of the rate of hydrolysis by 0.1*N*-hydrochloric acid of the acetates of β -chloro*isopropyl*, $\beta\beta'$ -dichloro*isopropyl*, $\beta\gamma$ -dichloro- and $\beta\gamma$ -dibromo-propyl alcohols. As in the case of β -substituted ethyl acetates, it is found that the presence of a halogen atom in the β -position retards hydrolysis, the influence being still more pronounced in the case of $\beta\gamma$ -disubstituted esters, but most striking in the case of esters with two halogens in the β - and β' -positions.

The esters were obtained as follows: $\beta\beta'$ -dichloro*isopropyl* acetate, b. p. 201—203°, by the action of acetyl chloride on $\beta\beta'$ -dichlorohydrin; $\beta\gamma$ -dichloropropyl acetate, b. p. 197—198°, in a similar manner, the alcohol being formed by chlorinating allyl alcohol; β -chloro*isopropyl* acetate, b. p. 149—150°, in the same way, the alcohol being obtained by adding concentrated sulphuric acid to allyl chloride at 0°, and then, after keeping a day, diluting with water and boiling, thus: $\text{CH}_2\text{:CH}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightarrow \text{CH}_2\text{Cl}\cdot\text{CHMe}\cdot\text{SO}_3\cdot\text{OH} \xrightarrow{\text{H}_2\text{O}} \text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\text{Cl} + \text{H}_2\text{SO}_4$; the alcohol is isolated by distilling the solution (up to 130°), neutralising the distillate with potassium carbonate, saturating with salt, and extracting with ether.

In the preparation of allyl chloride by the action of phosphorus trichloride on allyl alcohol, advantage may be taken of the insolubility of the chloride in water to separate it from the phosphorous acid.
J. C. W.

Preparation of *iso*Butyl Oleate. ERNST PREISWERK (Brit. Pat., 123685).—*iso*Butyl oleate, prepared by condensing oleic acid or its chloride with *isobutyl* alcohol by the usual methods, has b. p. 190°/4 mm. and D_{20}^{20} 0.86. It is insoluble in water and possesses healing properties in cases of tuberculosis.

Hydrolysis of Glycollide and Lactide in Acid Solution. HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1919, 52, [B], 745—752).—Glycollide and lactide are hydrolysed by water to glycollic and lactic acids with intermediate formation of glycollo-glycollic and lacto-lactic acids respectively: $\text{O} \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} \text{O} + \text{H}_2\text{O} = \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$; $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} + \text{H}_2\text{O} = 2\text{OH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The authors have particularly investigated the first phase of the reaction, since the second is known to proceed normally. It occurs too rapidly in alkaline solution to permit accurate measurement. In moderately acid solution, the change takes the form of two independent, simultaneous reactions, only one of which is catalysed by hydrogen ions.

It therefore appears that hydrolytic fission of β -lactones is catalysed slightly or not at all by hydrogen ions, that of γ -lactones is catalysed, whilst the opening of the six-membered ring of glycolide or lactide proceeds either with or without catalytic assistance of hydrogen ions.

The experiments were carried out by adding solutions of glycolide or lactide in anhydrous acetone to water or dilute acid at $19.8 \pm 0.1^\circ$; at suitable intervals, aliquot portions of the solution were added to a solution of potassium iodide and potassium iodate, and the liberated iodine was estimated by titration with sodium thiosulphate after allowing sufficient interval for the complete liberation of iodine. The results are probably slightly low, the error, however, not exceeding 1%. The presence of acetone does not affect the titration, whilst the secondary hydrolysis of the ester acid occurs so slowly that it need not be taken into account.

H. W.

The Basic Properties of Oxygen in Organic Acids and Phenols; and the Quadrivalency of Oxygen. JOSEPH KNOX and MARION BROCK RICHARDS (T., 1919, 114, 508—531).

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. VIII. On the Spontaneous Fission of Racemic Potassium-Cobalti-oxalate into its Optically Active Antipodes. F. M. JAEGER and WILLIAM THOMAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 693—706).—When an aqueous solution of inactive potassium cobalti-oxalate is allowed to crystallise at temperatures near 0° , the racemic salt separates in the form of dark green, almost black triclinic pinacoidal crystals of the composition $K_3\{Cr(C_2O_4)_3\}3\frac{1}{2}H_2O$, D^{15}_D 1.877. These crystals are not isomorphous with those of the corresponding triclinic chromium, rhodium, and iridium salts, the water content being different (A., 1918, i, 3). When, however, the inactive solution is allowed to crystallise near 18° , separate crystals of the *d*- and *l*-compounds are deposited. These have trigonal trapezohedral symmetry, and are isomorphous with the corresponding optically active rhodium and iridium salts: $\alpha:c=1:0.8968$, α $100^\circ 27'$, D^{15}_D 1.8893. Only on rare occasions could the *d*- and *l*-crystals be distinguished by the presence of hemihedral faces, in spite of their enormous optical activity. This is the first fully substantiated example of the spontaneous fission into its components of such a racemic complex metallic compound. The transition temperature of the racemic compound into its components, determined by the solubility method, was found at 13.2° .

The dark green solution of the active salt shows a pronounced absorption band between 5510 and 6520 Å.U. The form of the rotatory dispersion curve is noteworthy. The molecular rotation increases rapidly with increasing wave-length, but in the vicinity of the absorption band falls steeply, assuming the opposite algebraic sign at about 6260 Å.U., and reaching a maximum in the other

direction at about 6400 Å.U. The curve is similar in type to that of potassium chromium oxalate, the latter, however, showing a much greater absolute rotation on either side of the zero line. The positions of the maxima and minima are also different in the two salts, corresponding with the different positions of the absorption bands. For certain wave-lengths, the two *d*-forms (or *l*-forms) actually have opposite rotations. The influence of the specific nature of the central metallic atom is shown in the fact that the potassium rhodium- and iridium-oxalates have normal rotatory dispersion curves.

E. H. R.

The Supposed Diastatic Properties of Formaldehyde. HERMANN SALLINGER (*Ber.*, 1919, 52, [B], 651—656).—A further contribution to the controversy on this subject (compare Woker, A., 1917, i, 61, 447; Kaufmann, A., 1917, i, 251). The author considers that the only valid evidence of the enzymatic indifference of formaldehyde towards starch is obtained by observation of the specific rotation and absence of reducing power towards Fehling's solution which can be ascribed to the action of formaldehyde on starch. With regard to the first point, a solution of amylopectrin (Lintner) is found to retain its optical activity unchanged after digestion with formaldehyde during forty-four hours at 37°, thus confirming Kaufmann's previous observation. With regard to the second point, a solution of soluble starch (Wolff, Fernbach), after treatment with formaldehyde and removal of the latter as completely as possible, only showed slight reducing power towards Fehling's solution, which depended on traces of residual formaldehyde. Further, in a comparative series of experiments in which formaldehyde solutions of differing concentration were mixed on the one hand with starch solution and on the other with water, and subsequently treated with Fehling's solution, a greater reduction was not found in any instance in the solutions containing starch than in those from which it was absent. The author therefore considers formaldehyde to be enzymatically indifferent to starch.

H. W.

The Relations between the Chemical Structures of Carbonyl Derivatives and their Reactivities toward Salts of Semicarbazide. ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1919, 41, 393—424).—The velocities of the reactions of aldehydes and ketones with various reagents have been investigated quantitatively, chiefly by Petrenko-Kritschenko, and the results discussed in their theoretical aspects (see Stewart, "Stereochemistry," 474—501). The velocity factor in such reactions depends mainly on the magnitude of the free chemical energy of the carbonyl group and on its affinity relationships to the component parts of the reagent. From a determination of the reaction velocities of different ketones towards the same agent, conclusions may be drawn as to the influence of structure on the free energy of the carbonyl group, but this is not necessarily the same as discussing the reactivity of the

*m**

ketone. Reactivity is frequently confused with instability, but the latter term should be restricted to the behaviour of a compound towards physical forces, and the former used only in reference to the behaviour of a certain atom or group of atoms in a given chemical system. The reactivity of a ketone, for example, is the sum total of the changes in the free and bound chemical energy in all the atoms, manifesting itself at the carbonyl group because the hindrance to chemical change is best overcome at this point.

The present investigation has for its chief aim the arrangement of groups of carbonyl derivatives according to the relative reactivities of the members towards certain reagents. For such a purpose, semicarbazide is the most suitable agent, since its salts are only slightly hydrolysed in solution and most semicarbazones are only sparingly soluble in water. As a preliminary to the formation of a semicarbazone from a salt of semicarbazide, a carbonyl derivative must liberate the base, that is, it must exert as much energy as was dissipated in the neutralisation of the base by the acid. Since semicarbazide is a strong base, this energy will stand in direct relation to the affinity constant of the acid. The reactivity of a carbonyl compound can therefore be gauged by finding at what limit it ceases to react with a series of semicarbazide salts. Some carbonyl derivatives react with salts of semicarbazide and the strongest mineral acids. In such cases, the limit is ascertained by adding some of the free acid and finding how much is necessary to prevent reaction, or, in other words, to make the reverse hydrolysis of the semicarbazone to proceed with equal velocity. A similar method is employed in the case of two carbonyl derivatives which both react with the semicarbazide salt of one acid, but not with the salt of the next stronger acid; the more reactive compound is the one which forms a semicarbazone in the presence of the greater amount of the free acid.

Semicarbazide, m. p. 95° , and the following salts were employed in the experiments: hydrochloride, m. p. 175° ; hydrogen sulphate, m. p. 145° (decomp.); sulphate, m. p. 143° ; formate, m. p. 126° ; benzenesulphonate, plates, m. p. 187° (decomp.); acetate, m. p. 75° ; chloroacetate, m. p. $111-112^{\circ}$; dichloroacetate, m. p. 108° ; trichloroacetate, m. p. 154° (decomp.); oxalate, m. p. 133° (decomp.); maleate, m. p. 100° ; hydrofluoride; salicylate, m. p. 153° ; *o*-nitrobenzoate, m. p. 96° .

These salts and mixtures of them with the free acids fall into the following order when the difficulty of a ketone to liberate and react with the base is considered: (1) free base; (2) acetate, (3) formate; (4) chloroacetate; (5) oxalate; (6) dichloroacetate; (7) dichloroacetate + $0.5N$ -acid; (8) trichloroacetate; (9) hydrochloride; (10) hydrochloride + $0.2N$ -HCl; (12) hydrochloride + $0.5N$ -HCl; (13) hydrochloride + $0.6N$ -HCl; (15) hydrochloride + $1.0N$ -HCl. This order, therefore, may be regarded as the scale of reactivity.

In the first series of experiments, the reactions between aliphatic ketones and these agents in aqueous solution are described. For

the purpose, 0.5 mg.-mol. of the ketone was shaken with 0.8 c.c. of a solution containing 0.56 mg.-mol. of the salt, and any precipitates were purified and examined. No experiment was considered negative under 200 hours. The origins of the ketones are summarised, and the results are described in detail, discussed at some length, and reproduced by curves, particular attention being paid to the influence of branched chains. The least reactive ketone is propyl isopropyl ketone (1 on the scale), and the most reactive are methyl hexyl (12) and methyl octyl ketones (15). Dimethyl, diethyl, and dipropyl ketones come about 6 on the scale.

In a second series of experiments, alcoholic media were employed, 0.5 mg.-mol. of the ketone in 0.85 c.c. of alcohol of D 0.9270, or 0.9097 for the highest members, was shaken with 0.5 mg.-mol. of the reagent in the same volume of the same alcohol, and then at different intervals up to five months a few drops of the solution were evaporated and tested for a semicarbazone. Under such conditions, practically all the ketones only react with the free base; only the higher members, such as methyl hexyl ketone (10), show any great reactivity. The insolubility of the semicarbazone is obviously of considerable importance, but even in these cases in which the mixture remains homogeneous there is no connexion between reactivity and reaction velocity. Methyl hexyl ketone, for example, has the largest reactivity with semicarbazide in alcohol, but the velocity of its reaction with phenylhydrazine is only about half, and its velocity with potassium hydrogen sulphite about one-quarter, of the acetone velocities.

Acetophenone takes the ninth place on the scale and propiophenone about the fourth.

With the aldehydes, the outstanding feature is the great reactivity of formaldehyde and the aromatic aldehydes. These all react with semicarbazide hydrochloride even in the presence of 10*N*-hydrochloric acid. The changes from $\text{H}\cdot\text{CHO}$ to $\text{Me}\cdot\text{CHO}$ and $\text{C}_6\text{H}_5\cdot\text{CHO}$ to $\text{C}_6\text{H}_5\cdot\text{COMe}$ are accompanied by great falls in reactivity.

Several ketonic esters have also been investigated. Ethyl acetoacetate is much more reactive than the alkylacetoacetates, $\text{COMe}\cdot\text{CHR}\cdot\text{CO}_2\text{Et}$ and $\text{COMe}\cdot\text{CR}_2\cdot\text{CO}_2\text{Et}$, and is more reactive than ethyl benzoylacetate.

The following appear to be new: *methyl octyl ketone semicarbazone*, m. p. 119°; *ethyl methylacetoacetate semicarbazone*, pale blue crystals, m. p. 183—187° (decomp.); *ethyl ethylacetoacetate semicarbazone*, m. p. 154° (decomp.); *ethyl dimethylacetoacetate semicarbazone*, m. p. 183—187° (decomp.); *ethyl allylacetoacetate semicarbazone*, m. p. 125°; *ethyl diacetylmalonate semicarbazone*, $\text{C}_{13}\text{H}_{22}\text{O}_6\text{N}_6$; *ethyl oxaloacetate semicarbazone*, m. p. 162°; *ethyl benzoylacetate semicarbazone*, m. p. 125° (decomp.).

Some practical applications of the above classification of the ketones may be mentioned. In the first place, a scheme for the separation of a mixture of ketones could be designed, based on the treatment of the mixture with solutions of semicarbazide salts in

decreasing order of the strengths of the acids. Secondly, strong acids may be classified according to their reactivities in concentrated solutions by finding what excess of acid is necessary to inhibit the formation of the semicarbazone of a suitable ketone.

J. C. W.

Mutarotation of Dextrose and Lævulose. J. M. NELSON and FRANK M. BEEGLE (*J. Amer. Chem. Soc.*, 1919, **41**, 559—575).—The specific rotation of α -*D*-glucose, β -*D*-glucose, and β -*D*-fructose has been determined at 0.15°, 15°, 25°, and 37°. The values found are: α -*D*-glucose, +111.2°; β -*D*-glucose, +17.5°; and β -*D*-fructose, -130.8°. These values are constant for all the temperatures investigated. The relation between the rate of mutarotation of the three sugars and varying concentrations of hydrogen ion has been determined. It is shown that the equilibrium rotation of dextrose is not affected by temperature, whilst that of lævulose varies with the temperature of the solution. The mutarotation of dextrose appears to be simply racemisation, whilst that of lævulose is not. The mutarotation of dextrose and lævulose in the presence of each other and in the presence of sucrose and invertase has been measured, and in each case was found to be independent of the other when present, except in the case of solutions of lævulose and sucrose, when the rate of mutarotation and the rotation at equilibrium were affected. The temperature-coefficient of the mutarotation was also determined.

J. F. S.

Glycollonitrile-*D*-glucoside, $C_6H_{11}O_5 \cdot O \cdot CH_2 \cdot CN$. EMIL FISCHER (*Ber.*, 1919, **52**, [B], 197—200. Compare A., 1917, i, 658).—The isolation of *glycollonitrile-D-glucoside* by the hydrolysis of its tetra-acetyl derivative with methyl-alcoholic ammonia is now described. It is an amorphous substance, $[\alpha]_D^{19} -45.97^\circ$, which is soluble in cold water or pyridine, but not in most indifferent organic media, and it is very susceptible to hydrolytic influences. It is not so readily affected by emulsin, however, as mandelonitrile glucoside is, the best conditions being when the *H*-ion concentration is about $10^{-5.2}$. Hydrogen cyanide is formed during the hydrolysis. Proof of the purity and identity of the compound lies chiefly in its re-acetylation to tetra-acetylglucosidoglycollonitrile.

J. C. W.

Syntheses of Linamarin and Glycollonitrile Celloside. EMIL FISCHER and GERDA ANGER (*Ber.*, 1919, **52**, [B], 854—868).—The synthesis of linamarin, effected on lines similar to those followed by Fischer and Bergmann (A., 1917, i, 657) in the syntheses of mandelonitrile glucoside and sambunigrin, has already been described (A., 1918, i, 526).

Ethyl tetra-acetylglucosido- α -hydroxyisobutyrate is converted by aqueous barium hydroxide into *glucosido- α -hydroxyisobutyric acid*, prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20} -23.06^\circ$ in water. The physical constants of the synthetic linamarin differ slightly from those recorded for the natural substance, particularly in respect

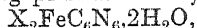
to optical activity, but the differences are not sufficiently great to cause any doubt as to the identity of the products. Both the synthetic and natural glucosides are slowly hydrolysed by emulsin, more rapidly by phaseolunataase from *Phaseolus lunatus*. The substance is in all probability a β -glucoside, since it is the result of a type of synthesis which in all previous instances has led to β -glucosides, and since all the successive products are lævorotatory, whilst, in general, the α -glucosides are dextrorotatory.

Since amygdalin, the most important representative of the cyanogenetic glucosides, is a derivative of a disaccharide, the authors have extended the synthesis to similar sugars, and have prepared the compound of cellulose with glycollonitrile on lines similar to those used for linamarin.

Ethyl hepta-acetylcellosidoglycollate, needles, m. p. 161—163° (corr.), $[\alpha]_D^{17} - 30.9^\circ$ in acetone, is prepared from acetobromocellulose, ethyl glycollate, and dry silver oxide, and is converted by methyl-alcoholic ammonia into *cellosidoglycollamide*, prisms, m. p. 150—152° (corr.), $[\alpha]_D^{17} - 27.9^\circ$ in water, which is hydrolysed by emulsin with the formation of dextrose. The amide is converted in the usual manner into *cellosidoglycollamide hepta-acetate*, slender needles, m. p. 205—206° (corr.), $[\alpha]_D^{18} - 20.6^\circ$ in acetone, which, when treated with phosphorus oxychloride, passes into *cellosidoglycollonitrile hepta-acetate*, small needles, m. p. 200—202° (corr.) after previous softening, $[\alpha]_D^{18} - 26.68^\circ$ in acetone. The latter, on deacetylation, gives *cellosidoglycollonitrile*, $\text{CN} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{C}_{12}\text{H}_{21}\text{O}_{10}$, which could only be obtained as an amorphous mass, frequently of a pale yellow colour; when heated, it softens at about 80°, and is slowly converted into a viscous mass, which evolves gas at about 108°. It has $[\alpha]_D^{18} - 28.74^\circ$ in water. When reacylated by acetic anhydride in pyridine solution, it gives the original hepta-acetate in good yield. It is hydrolysed by emulsin with comparative ease, giving hydrocyanic acid and dextrose. H. W.

Alkylaminochromi-compounds. III. H.J. MANDAL (Ber., 1919, 52, [B], 330—341. Compare A., 1916, i, 202, 792).—The following *chloropentapropylaminochromic* salts are described: The *chloride*, $[\text{CrCl}(\text{NH}_2\text{Pr})_5]\text{Cl}_2$, is obtained by the action of propylamine on chromic chloride at as low a temperature as possible, a dichlorotetrapropylaminochromic chloride being formed if the reaction is not well controlled. It crystallises in red tablets from water, in which 1 part is soluble in 35 parts at the ordinary temperature, and it gives up propylamine at 60—70°. Other salts are prepared as precipitates from the red solution of the chloride by double decomposition or addition of a suitable chloride. The *bromide* requires nearly twice, and the *iodide* nearly three times, as much water for solution. The *mercurichloride*, $5\text{XCl}_2 \cdot 4\text{HgCl}_2$, is pale violet; the *mercuribromide*, XHgBr_4 , is very pale reddish-violet; the *mercuri-iodide*, XHgI_4 , is still paler; the *platinichloride*, $\text{XPtCl}_6 \cdot \text{H}_2\text{O}$, has the colour of chamois; the *bismuthichloride*, $\text{X}_3\text{Bi}_2\text{Cl}_{12}$, is a pale reddish-violet powder; and

the *stibichloride*, XSbCl_3 , forms very minute, indefinite crystals. The *hydrogen sulphate*, $\text{X}(\text{HSO}_4)_2$, crystallises in glistening, violet scales; the *dithionate*, XS_2O_6 , forms violet, hexagonal tablets; and the *sulphide*, XS_3 , is a yellowish-brown powder. The *nitrate*, $\text{X}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, forms long prisms. The *ferrocyanide*,



is pale red, but becomes yellowish-brown in the light, and is about the most insoluble salt of the series; the *ferricyanide*, $\text{X}_3(\text{FeC}_6\text{N}_6)_2$, is yellow with a tinge of red, and the *chromicyanide*, $\text{X}_3(\text{CrC}_6\text{N}_6)_2$, is a reddish-violet, microcrystalline powder. The *trioxalocobaltiate*, $\text{X}_3[\text{Co}(\text{C}_2\text{O}_4)_3]_2$, is a bluish-green, crystalline powder, and the *trioxalochromiate*, $\text{X}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]_2$, crystallises in brownish-violet, glistening bundles of minute needles. The dichromate is soluble, but the *chromate*, XCrO_4 , is a very sparingly soluble, yellow powder.

J. C. W.

Xanthates of Quaternary Ammonium, Sulphine, and Analogous Bases. JAIME FERRER (*Anal. Fis. Quim.*, 1918, 16, 724—727).—Quaternary ammonium bases react with carbon disulphide in a manner similar to alkali hydroxides, giving xanthates. In a preliminary note, the author describes the preparation of the xanthates of quaternary ammonium, sulphine, and iodonium bases, giving some quantitative details of their properties. Tetramethylammonium hydroxide was dissolved in ethyl alcohol, and carbon disulphide added. On evaporation, the *xanthate* is obtained in yellow, hygroscopic needles, soluble in ether and acetone. With propyl alcohol, the corresponding xanthate is obtained in plates.

Phenyltrimethylammonium ethyl- and propyl-xanthates were prepared similarly, crystallising in needles. Solutions were obtained giving xanthate reactions by adding disulphide to alcoholic solutions of methylpyridinium hydroxide and methylveratrinium hydroxide.

Triethylsulphine hydroxide was dissolved in ethyl, propyl, and isobutyl alcohols. On treatment with carbon disulphide and evaporation, the corresponding *xanthates* were obtained in yellow needles soluble in water.

Diphenyliodonium hydroxide gives a *xanthate* crystallising in brilliant needles, only slightly soluble in water, alcohol, and ether.

By similar methods, *methylstibonium ethylxanthate* (colourless crystals) and *ethylmercury ethylxanthate* were prepared.

W. S. M.

Constitution of Methyloxaluric Acid. ROBERT BEHREND (*Ber.*, 1919, 52, [B], 424—426).—Only one of the two possible methyloxaluric acids is known, but its constitution has not been determined hitherto (compare Henkel, A., 1911, i, 159). Its ethyl ester, flat prisms, m. p. 144—146°, has now been heated with acetyl chloride in a sealed tube at 120—130°, and the following products have been isolated and fully identified: (a) much methylparabanic acid, (b) a small quantity of the acetyl derivative of this, and

(c) a little acetoxamethane. The last substance gives the clue to the constitution of the methyloxaluric acid, for it may be supposed to be formed according to the equation $\text{NIIme} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CO}_2\text{Et} + \text{AcCl} = \text{NHAc} \cdot \text{CO} \cdot \text{CO}_2\text{Et} + \text{CH}_3 \cdot \text{N} \cdot \text{CO} + \text{HCl}$. J. C. W.

Action of Halogenates and Hypohalogenites on Mercury Fulminate. A. LANGHANS (*J. pr. Chem.*, 1918, [ii], 98, 255—314).—The action of halogenates and hypohalogenites on mercury fulminate has been studied under various conditions; more definite quantitative data are promised in a subsequent paper, but the results already obtained are considered to furnish further evidence for the oxime structure for fulminic acid.

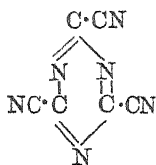
The action of potassium chlorate and potassium bromate solutions on mercury fulminate in the presence of hydrochloric acid depends greatly on the conditions of the experiment, and the original memoir must be consulted for details. Generally, it may be said that bromate acts more energetically than chlorate, and that for the production of the maximum amount of blue, oily product a definite relationship between the concentrations of hydrochloric acid and bromate must be maintained, and that the quantity of mercury fulminate is definitely related to that of the other reagents.

Mercury fulminate is decomposed by potassium hypochlorite solution, yielding chiefly mercuric oxide, which is only produced in small amount by hypobromite or hypoiodite. The action of potassium hypobromite yields varying products, according to experimental conditions, a summary of which is impossible until more exact data have been obtained; the most remarkable product is a deep blue oil, which is best obtained by the gradual addition of moist mercury fulminate to a solution of bromine in 10% potassium hydroxide, 7—8 c.c. of bromine being used for each 10 grams of potassium hydroxide; it has D 2.6844 or 2.6852, and is unstable towards light, but more stable in the dark. It consists in all probability of *bromonitrosomethane*. It decomposes when distilled under ordinary pressure, evolving brown vapours and yielding distillates, which generally crystallise after a time. It yields crystalline products when treated with the following reagents: sodium sulphite or sodium hydrogen sulphite (colourless leaflets, m. p. 91—92° [uncorr.] after softening at 89°); sodium thiosulphate; potassium cyanide (m. p. 55°); ammonium persulphate (m. p. 68°); silver nitrate (colourless leaflets, m. p. 67°); phenylhydrazine; furfuraldehyde (m. p. above 200°); benzoyl peroxide (colourless needles); hexamethylenetetramine (yellow or white solid, m. p.'s 95° and 187° respectively, according to conditions of experiment); benzenesulphonic acid; picric acid; sodium xanthogenate; glycine (m. p. 65°). The blue compound is not formed when bromine acts on mercury fulminate in the presence of acetic anhydride, glacial acetic acid, or pyridine.

A sensitive method for the detection of mercury fulminate in fuse compositions is founded on the production of the blue oil.

H. W.

Simple Cyanic and Cyanuric Compounds. I. Hexacyanogen [Cyanuric Cyanide]. ERWIN OTT (*Ber.*, 1919, 52, [B], 656—665).—*Hexacyanogen* (annexed formula) is obtained by heating a mixture of cyanuric tricarboxylamide and phosphoric oxide in a vacuum rapidly to 210—220°, and finally to about 250°. The yield is about 17%.



The substance forms monoclinic crystals ($a:b:c = 0.9233:1:1.0688$, $\beta = 90^\circ 26'$), has m. p. 119° , b. p. 262° (corr.)/771 mm., $119^\circ/0.5$ —1 mm. It separates from benzene + $1C_6H_6$. When the vapour is led over a strongly heated platinum wire, it is quantitatively depolymerised to dicyanogen. It is very sensitive to moisture. It slowly dissolves in water at 0° , and two cyanogen groups are rapidly eliminated in the form of hydrogen cyanide, whilst the third cyanogen group is removed at a slightly higher temperature, cyanuric acid being formed. In virtue of the three conjugated double linkings, it seems probable that water is first added and hydrogen cyanide subsequently eliminated from the hydroxynitrile thus formed. With methyl alcohol, reaction proceeds more slowly, and can be arrested by suitable adjustment of experimental conditions at any of the three stages theoretically possible. There are thus obtained: (1) the *monomethoxydinitrile*, $OMe \cdot C_3N_3(CN)_2$, colourless leaflets, m. p. 86.5° , (2) the *dimethoxymononitrile*, prisms, m. p. 21° , and (3) trimethyl cyanurate, m. p. 135° . A solution of hexacyanogen in carbon tetrachloride does not visibly react with chlorine even in the presence of iodine, but the odour of cyanuric chloride shows some action to occur; it also appears to be indifferent to hydrogen chloride.

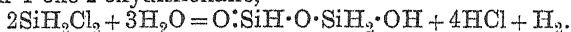
H. W.

Silicon Hydrides. VI. Chlorination and Methylation of Monosilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1919, 52, [B], 695—724. Compare A., 1916, ii, 319; 1917, ii, 110, 111, 353, 361).—Whilst monosilane does not react with hydrogen chloride in the absence of a catalyst at 200° , reaction occurs slowly in the presence of aluminium chloride at the ordinary temperature, and with reasonable rapidity at 100° ; when the gases are used in molar proportions, the chief product is monochlorosilane, whilst with the double proportion of hydrogen chloride, *dichlorosilane* is chiefly formed, the action in this respect differing somewhat considerably from that with hydrogen bromide.

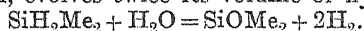
Chloromonosilane is a non-spontaneously inflammable gas, m. p. -118° , b. p. -30.5° , D- 113° 1.145 (as liquid). It is immediately decomposed by water, yielding disiloxane; protracted action of water causes hydrolysis with evolution of hydrogen. It reacts with gaseous zinc methyl, yielding exclusively *methylmonosilane*, SiH_3Me , b. p. -57° , m. p. -156.5° , which is scarcely attacked by water in the absence of alkali, but is slowly decomposed by alkali in accordance with the equation $SiH_3Me + 2H_2O = [SiO(OH)Me]_x +$

3H_2 . Further chlorination of methylsilane by means of hydrogen chloride and aluminium chloride leads to the production of *methylchloromonosilane* and *methyldichloromonosilane*, which can be separated by protracted fractional distillation. The former is a colourless gas, m. p. 134° , b. p. ca $+7^\circ$, $D_{20}^{20} 0.935$ (as liquid), which is very sensitive to moisture; evidence that the chlorine atom is attached to silicon is afforded by converting it into dimethylsilane by the action of zinc methyl, the product being identical with that prepared from dichlorosilane. Dichloromethylmonosilane was isolated in approximately pure condition.

Dichloromonosilane is obtained as a by-product in the preparation of the monohalogen derivative by further chlorination of chloromonosilane by aluminium chloride and hydrogen chloride, and by the action of hydrogen chloride (2 mols.) on monosilane (1 mol.); in the latter case, the main product is the dichloro-derivative mixed with a little monochloro-product and unchanged hydrogen chloride and very little trichloromonosilane. It has m. p. -122° , b. p. 8.5° , and is particularly sensitive to moisture and fat. With water, it immediately yields prosiloxane, $\text{SiH}_2(\text{:O})$, and then 1-oxo-2-oxydisiloxane,



It is converted by thorough treatment with gaseous zinc methyl into dimethylmonosilane, SiH_2Me_2 , m. p. -150° , b. p. -20° , which, with alkali, evolves twice its volume of hydrogen,



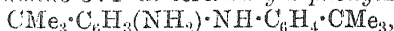
The dimethylprosilo-xane is soluble in an excess of alkali, probably yielding $\text{SiMe}_2(\text{ONa})_2$; acids precipitate an oil from this solution which slowly becomes partly solid, and consists of a mixture of SiMe_2O , $\text{SiMe}_2(\text{OH})_2$, and their condensation and polymerisation products.

It is noticeable that the displacement of hydrogen by chlorine in silicon derivatives has much less influence in raising the boiling and melting points than with derivatives of carbon. H. W.

Nitration of *tert.*-Butylbenzene. D. F. DU TOIT MALHERBE (*Ber.*, 1919, 52, [B], 319—324).—When *tert.*-butylbenzene is left with nitric acid ($D 1.5$), it is almost entirely converted into *p*-nitro-*tert.*-butylbenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CMe}_3$, an oil which does not crystallise in a freezing mixture, having b. p. $142\text{—}143^\circ/17\text{ mm.}$, whilst a dinitro-derivative, pale yellow prisms, m. p. $61\text{—}62^\circ$, b. p. $185^\circ/15\text{ mm.}$, is formed at 60° (Baur, A., 1894, i, 445).

The constitution of the mono-nitro-compound does not agree with Senkowski's statements (A., 1890, 1296). It has been proved as follows: (a) oxidation with dilute nitric acid at 130° to *p*-nitrobenzoic acid; (b) reduction to *p*-*tert.*-butylaniline, and conversion into its acetyl, benzoyl, and dimethyl derivatives, and into *p*-*tert.*-butylphenol; (c) reduction by sodium methoxide solution to *p*-azoxy-*tert.*-butylbenzene, pale yellow leaflets, m. p. 138° ; (d) reduction to *p*-azo-*tert.*-butylbenzene, orange-red needles, m. p. 183° , and the hydrazo-compound by means of aqueous-alcoholic

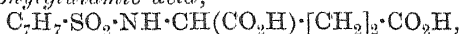
potassium hydroxide and zinc dust; (c) the semidine transformation of the hydrazo-derivative, by means of alcoholic stannous chloride, into 6-amino-3:4'-di-tert.-butyldiphenylamine,



white leaflets, m. p. 100--101°. As an *o*-aminodiphenylamine, the latter base reacts with benzil to form a *stilbazonium* compound, $\text{C}_{34}\text{H}_{36}\text{ON}_2$, greenish-yellow needles, m. p. 165--167° (Taüber, A., 1892, 853), and with benzaldehyde to give a *benzenyl* compound, $\text{C}_{27}\text{H}_{32}\text{N}_2$, slender, yellow needles, m. p. 126--127° (*ibid.*).

J. C. W.

New Compounds of Glutamic Acid. PETER BERGELL (*Zeitsch. physiol. Chem.*, 1919, **104**, 182--188).—*β*-Naphthalenesulphonylglutamic acid, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{H})\cdot[\text{CH}_2]_2\cdot\text{CO}_2\text{H}$, crystallises in microscopic needles from water, m. p. 165° (uncorr.). *Toluenesulphonylglutamic acid*,



forms woolly masses of soft, short needles, m. p. 115--117° (uncorr.). The presence of 1% of glutamic acid or glycine in urine may be detected by the isolation of their *β*-naphthalenesulphonyl derivatives.

J. C. D.

Formation of Diphenyl by the Action of Cupric Salts on Organometallic Compounds of Magnesium. JACOB KRIZEWSKY and EUSTACE EBENEZER TURNER (*T.*, 1919, **114**, 559--561).

Transformation of Quaternary Ammonium Salts into Tertiary Amines with Sodium Ethoxide. D. VORLÄNDER and ELISABETH SPRECKELS (*Ber.*, 1919, **52**, [B], 309--311).—Aromatic primary amines can be readily converted into a mixture of the dimethyl derivatives and the corresponding quaternary salts by treatment with an excess of methyl sulphate and alkali. A convenient process for transforming the quaternary salts into the tertiary bases has now been found. The crude product is saturated with hydrochloric acid, evaporated to dryness, and the mixed salts are boiled under reflux with a solution of sodium (two or three equivalents) in alcohol (50--100 parts) for three to five hours. From 85 to 95% of the quaternary salt is converted into the tertiary amine.

The process has not been fully tested in the case of aliphatic bases, but more concentrated solutions of sodium ethoxide, or perhaps amyloxide, appear to be necessary.

J. C. W.

Oxidation of *o*-Tolyltrimethylammonium Salts to *o*-Benzobetaine. D. VORLÄNDER and FRANZ JANECKE (*Ber.*, 1919, **52**, [B], 311--314).—The oxidation of *o*-tolyltrimethylammonium methyl sulphate (Ullmann, A., 1903, i, 395) to *o*-benzobetaine (Willstätter, A., 1904, i, 235) by means of permanganate is described. In addition to the hydriodide, aurichloride, and free base already obtained by Willstätter, the authors have prepared the *hydro*-

chloride, $C_{10}H_{14}O_2NCl \cdot H_2O$, jagged leaflets, m. p. $170-176^\circ$. When boiled with a solution of sodium ethoxide, the base deposits the sodium salt of *N*-dimethylantranilic acid in felted needles. The free acid corresponds with Willstätter's description (*ibid.*), and forms a *hydriodide*, m. p. 180° (decomp.), a *periodide*, m. p. 163° (decomp.), and a *platinichloride*, m. p. 198° (decomp.).

J. C. W.

Nitration of Benzotrichloride. ELISABETH SPRECKELS (*Ber.*, 1919, 52, [B], 315—319).—Under the usual conditions of nitration, benzotrichloride yields nitrobenzoic acids, but if treated with a solution of nitrogen pentoxide in carbon tetrachloride at -10° , a mixture of nitrobenzotrichlorides is formed almost free from nitrobenzoic acids and unchanged material. About 80% of the mixture has b. p. $150-153^\circ/18$ mm. It is fairly stable towards water and cold dilute alkalis, much more so, in fact, than benzotrichloride itself, neither does it readily change into the nitrobenzoic acids in contact with cold, concentrated nitric acid. It is not, therefore, the precursor of the nitrobenzoic acids formed under the usual conditions.

The proportions of the isomerides in the mixture have been determined approximately by boiling with barium hydroxide and separating the barium salts of the nitrobenzoic acids. The main product is *m*-nitrobenzotrichloride, with about one-fifth of its weight of the *para*-compound, which is much more than benzoic acid yields. There is also a small quantity of the *ortho*-compound in the mixture.

J. C. W.

Phenylcarbamic Acid and its Homologues. F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 664—677).—The compound formed between aniline and carbon dioxide under pressure at low temperatures was examined by Ditte many years ago (*A.*, 1888, 49), and was found to contain the constituents in equimolecular proportions. This composition has now been confirmed and the conditions of its existence established. Within the limits of temperature and pressure of the experiments, four phases are possible—the solid compound, two liquids, and vapour. The four three-phase *P.-T.* curves have been determined and the point of intersection, the quadruple point, found at 18° with a pressure of 52.0 atm. The critical end-point lies at 37° , that is, 6° and about 7 atm. higher than the critical point of carbon dioxide.

Similar compounds are formed between carbon dioxide and the three toluidines. The quadruple points of the three compounds are as follows: *o*-toluidine, -7.5° , 27.5 atm.; *m*-toluidine, 6.3° , 39.2 atm.; *p*-toluidine, (1) 31.5° , 70 atm., (2) 29.7° , 44 atm. In the last case, there are two quadruple points; the first has the compound as the solid phase, whilst the second has *p*-toluidine and the compound both present as solid phases in equilibrium with one liquid and vapour. Whilst *o*-toluidine has the lowest quadruple

point, *m*-toluidine has the lowest melting point, but otherwise the quadruple and melting points follow the same order. The critical end-points lie close together, and the three-phase curves L_1L_2G (two liquids and vapour) are nearly coincident.

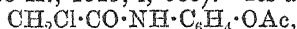
All the compounds contain base and carbon dioxide in molecular proportions, and are to be regarded as carbamic acids.

E. H. R.

Preparation of Phenol. H. H. Dow (U.S. Pat. 1274394).—Bromobenzene is converted into phenol by heating with a dilute alkali hydroxide solution in closed vessels under a pressure of 20 atmospheres. [See *J. Soc. Chem. Ind.*, June.] G. F. M.

Some Aromatic Amines and Chloroacetyl Derivatives. WALTER A. JACOBS, MICHAEL HEIDELBERGER, and IDA P. ROLF (*J. Amer. Chem. Soc.*, 1919, **41**, 458—474).—The compounds described in this communication are intermediate products in the preparation of several aromatic arsenic derivatives, which will be dealt with in a future series of papers.

An improved method for preparing *o*-chloroacetylaminophenol is described (compare A., 1915, i, 668). Its acetate,



obtained by the action of acetic anhydride and a drop of sulphuric acid, has m. p. 113.5—114.5°.

4-Chloroacetylaminoo-cresol, rhombic plates, m. p. 154—155°, and the more soluble 6-chloroacetylaminop-cresol, silky needles, m. p. 151—152.5°, are prepared from the aminocresols by the new way (A., 1917, i, 552).

1-Chloroacetylaminoo-β-naphthol forms very pale yellow, nacreous plates, m. p. 192—193° (decomp.), and 4-chloroacetylaminoo-α-naphthol crystallises in long, faintly purple, silky needles, m. p. 199.5—201.5°.

4:6-Dichloro-3-acetylaminophenol is obtained in silky needles, m. p. 233—236°, by chlorinating *m*-acetylaminophenol in acetic acid solution, and is hydrolysed by boiling with hydrochloric acid to 4:6-dichloro-3-aminophenol, large, striated prisms, m. p. 135—136°, which is converted into 4:6-dichloro-3-chloroacetylaminophenol, slender, interlaced needles, m. p. 185.5—186.5°. The 4:6-dichloro-3-acetylaminophenol is also methylated by means of methyl sulphate, and the 4:6-dichloro-3-acetanisidide, tufts of delicate needles, m. p. 157.5—159°, is hydrolysed to 4:6-dichloro-3-anisidine, which crystallises in creamy, rhombic prisms, m. p. 50.5—51.5° (corr.). The constitution of the compounds of this series is revealed by converting the latter base, by the diazo-reaction and application of methyl sulphate, into 4:6-dichloro-1:3-dimethoxybenzene (Auwers and Pohl, A., 1914, i, 981).

If the chlorination of *m*-acetylaminophenol is carried out without the precaution of shaking the acetic acid mixture, a good deal of 2:4:6-trichloro-3-acetylaminophenol is formed. This separates when the dilute acetic acid mother liquors from the dichloro-com-

pound are further diluted, and it crystallises in rhombic plates with $0.5\text{H}_2\text{O}$, or anhydrous needles, m. p. $185-186.5^\circ$.

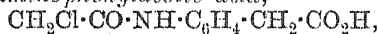
6-Bromo-3-acetylaminophenol is prepared by direct bromination and hydrolysed to 6-bromo-3-aminophenol (compare Heller, A., 1909, i, 568). 6-Bromo-3-chloroacetylaminophenol crystallises in rhombs, m. p. $191-193^\circ$.

m-Acetylaminophenol is also boiled with chloroacetic acid and concentrated sodium hydroxide, and thus converted into *m*-acetylaminophenoxyacetic acid, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which crystallises from water in slender needles with $1\text{H}_2\text{O}$, or from acetic acid in spherules, m. p. $170.5-172.5^\circ$. This is hydrolysed to *m*-aminophenoxyacetic acid (A., 1917, i, 695), and then converted into *m*-chloroacetylaminophenoxyacetic acid, spherules, m. p. $159-160^\circ$ (clear at 162°).

Considerable quantities of 4-aminoguaiacol were required for the preparation of catechol derivatives. This is obtained by coupling diazotised sulphanilic acid with guaiacol and reducing the crude dye with hydrogen sulphide in ammoniacal solution. *p*-Sulphobenzeneazoguaiacol crystallises from water in glistening, green needles and long, thin plates with $1\text{H}_2\text{O}$, decomp. above 220° . 4-Aminoguaiacol is hydrolysed by means of hydrobromic acid to the hydrobromide (flat needles or plates, decomp. $255-260^\circ$) of 4-aminocatechol, which crystallises from a mixture of alcohol and benzene in grey plates and clusters of short prisms, m. p. $124-125^\circ$ (decomp., purple residue). In the isolation and filtration of the base, air must be excluded as far as possible by a current of carbon dioxide. 4-Chloroacetylaminocatechol, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$, forms slender needles, m. p. $156-157.5^\circ$.

p-Chloroacetylaminooacetophenone crystallises as a woolly mass of needles from alcohol or leafy aggregates of plates from toluene, m. p. $152-153^\circ$ (corr.).

p-Chloroacetylaminophenylacetic acid,



forms a snowy mass of needles, m. p. $158-160^\circ$.

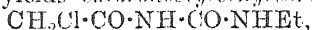
Ethyl chloroacetyl anthranilate, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, crystallises in glistening needles, m. p. $79.5-80^\circ$ (corr.), and changes into *ethyl iodoacetyl anthranilate*, transparent prisms, m. p. $78.5-79^\circ$ (corr.), when warmed with a solution of sodium iodide in acetone. *o*-Methylaminobenzoic acid yields *chloroacetyl-N-methylanthranilic acid*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, colourless spars, m. p. $167-168^\circ$ (corr.), the *ethyl* ester of which forms stout prisms, m. p. $50-51^\circ$ (corr.).

Sodium sulphanilate gives rise to *sodium chloroacetylsulphanilate*, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{Na}$, which crystallises in hair-like masses of needles, decomposing somewhat when dried at 100° .

3-Amino-*o*-phenolsulphonic acid, prepared by heating *m*-aminophenol with concentrated sulphuric acid at 100° , yields 3-chloroacetylaminoo-phenolsulphonic acid, minute plates and flat needles, not molten at 275° , the sodium salt of which crystallises as a voluminous mass of small needles with $0.5\text{H}_2\text{O}$.

Improvements in the preparation of chloroacetomethylamide and chloroacetopiperidide are described (compare A., 1915, i, 668). *Chloroaceto-n-propylamide*, $\text{CH}_3\text{Cl}\cdot\text{CO}\cdot\text{NHPr}^n$, has b. p. $105-106^\circ/10.5$ mm. (corr.), and forms a *hexamethylenetetraminium* salt, in stout, hexagonal plates, m. p. $147-149^\circ$.

Ethylcarbamide yields *chloroacetyl ethylcarbamide*.



in long needles, m. p. $141.5-142.5^\circ$ (corr.). J. C. W.

Catalytic Preparation of the Aminophenols and the Phenylenediamines. O. W. BROWN and L. L. CARRICK (*J. Amer. Chem. Soc.*, 1919, **41**, 436-440).—Mignonac (*Bull. Soc. chim.*, 1910, [iv], **7**, 270) described the reduction of the nitrophenols by passing a mixture of their vapours and hydrogen over nickel at $160-190^\circ$, but found that the production of the aminophenols was accompanied by the formation of ammonia, phenol, and aniline. This work is confirmed, and it is also reported that nickel is not so active when deposited on pumice as otherwise.

With finely divided copper, deposited on small pieces of pumice, the reduction is more efficient than with nickel, there being no by-products. Thus *o*- or *p*-nitrophenol and hydrogen passed over copper at $210-315^\circ$ (best, 265°) give practically quantitative yields of the pure white aminophenols, the more volatile product, of course, reacting more quickly. The *o*-aminophenol is obtained in plates when copper is used, but when reduced nickel is employed, it is formed in long needles with the same m. p. (170°), especially at the higher ranges of temperature.

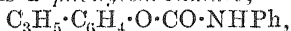
The nitroanilines, and especially *m*-dinitrobenzene, may be reduced in the same way to the phenylenediamines, but the process is too slow (owing to the slight volatility of the compounds) to be of much practical value, the only advantage being the high degree of purity of the products. J. C. W.

Transformation of Phenyl Allyl Ethers into the Isomeric Allylphenols. II. L. CLAISEN (*Annalen*, 1919, **418**, 69-120. Compare A., 1912, i, 965; 1913, i, 1175).—I. *Mono-, Di-, and Tri-allylation of Phenol* [with O. EISLEB and F. KREMERS].—*o*-Allylphenol, b. p. $220^\circ/760$ mm. or $99^\circ/12$ mm., D_4^{20} 1.0255, is obtained (1) by heating phenyl allyl ether in an atmosphere of carbon dioxide until the temperature is about 220° , heating for about six hours being necessary. (2) by heating 4-allyloxybenzoic acid with quinoline at 170° , and finally at the b. p. of the solution, (3) by heating 3-allylsalicylic acid with dimethylaniline slowly to the b. n. of the solution, (4) by boiling a mixture of methyl 3-allylsalicylate and aniline for four hours, and (5) least satisfactorily from 2-allyloxybenzoic acid. In the first method, a small quantity of 1-methylcoumaran is formed, which is removed by extraction with light petroleum after basifying the reaction product with 20% sodium hydroxide. Attempts to accelerate the transformation of phenyl allyl ether into *o*-allylphenol by catalysts were unsuccessful; alkalis had no effect, and acids only increased the amount of methyl-

coumaran, the addition of pyridine hydrochloride, for example, resulting in the production of this compound in 60% yield.

The position of the allyl group in *o*-allylphenol is proved (1) by heating with methyl-alcoholic potassium hydroxide, whereby Pauly and Buttler's *o*-propenylphenol is obtained, (2) by heating the methyl ether of the allylphenol with potassium hydroxide and oxidising the resulting *o*-propenylphenyl methyl ether, whereby *o*-methoxybenzoic acid is obtained, and (3) by coupling allylphenol with benzenediazonium chloride, the product being identical with the 4-benzeneazo-2-allylphenol obtained by the transformation of 4-benzeneazophenyl allyl ether (*loc. cit.*).

o-Allylphenol forms a *phenylcarbamate*,



colourless needles, m. p. 106—106·5°, methyl ether (*o*-esdragole), b. p. 207°/761 mm. or 86—87°/12 mm., D_{15}^{25} 0·9770 (the ozonide of which is very explosive and yields *o*-methoxyphenylacetaldehyde by treatment with glacial acetic acid and zinc dust), and acetate, b. p. 238·5—239°/757 mm. or 117—118°/15 mm.; the last derivative forms an oily *dibromide*, which is converted into 1-methylcoumarone by boiling with methyl-alcoholic potassium hydroxide.

To the list of substitution products of *o*-allylphenol already described (*loc. cit.*) is to be added 4:6-dichloro-*o*-allylphenol, b. p. 264°, D_{15}^{25} 1·288, which is very easily obtained by heating 3:5-dichloro-2-allyloxybenzoic acid, needles, m. p. 118° (decomp.); the methyl ester of this acid, $\text{C}_3\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_3\text{Cl}_2\cdot\text{CO}_2\text{Me}$, b. p. 160°/10 mm., is prepared by boiling methyl 3:5-dichlorosalicylate in methyl ethyl ketone solution with allyl bromide and potassium carbonate.

o-Propylphenol is obtained by reducing *o*-allylphenol by the Paal-Skita method, and also by reducing 3-allylsalicylic acid in a similar manner and heating the resulting 3-propylsalicylic acid, m. p. 91·5° (Spica gives 93—94°), with dimethylaniline at the b. p. of the solution until the evolution of carbon dioxide ceases. 2-Acetoxy-3-propylbenzoic acid (3-propylaspirin) crystallises in needles, m. p. 97—97·5°.

2:6-Diallylphenol, b. p. 256—257°/770 mm. (slight decomp.; in carbon dioxide) or 130°/15 mm., has D_{15}^{25} 0·9920, not 0·9905, as stated previously (*loc. cit.*). It is readily obtained by heating *o*-allylphenyl allyl ether, b. p. 104—105°/10 mm., D_{15}^{25} 0·9675 (prepared from *o*-allylphenol in acetone solution, allyl bromide, and potassium carbonate), for ten minutes in an atmosphere of carbon dioxide while the temperature rises from 235° to 256°, or, better, with half its weight of diethylaniline for thirty minutes while the temperature increases from 225° to 237°. It forms a *phenylcarbamate*, needles, m. p. 141—142°. Its constitution is definitely proved by the production of the compound by heating 4-hydroxy-3:5-diallylbenzoic acid (*loc. cit.*) with dimethylaniline at the b. p. for one to one and a-half hours. By hydrogenation in alcoholic solution, 2:6-diallylphenol yields 2:6-dipropylphenol, b. p. 256°/764 mm., m. p. 28° (*phenylcarbamate*, needles, m. p. 125°).

4-Allylphenol and 2:4-diallylphenol are not produced by the transformation of phenyl allyl ether and *o*-allylphenyl allyl ether respectively. The latter, b. p. 266—268°/750 mm. (*phenylcarbamate*, prisms, m. p. 88—88·5°), is obtained indirectly by heating 3:5-diallylsalicylic acid (*loc. cit.*) with dimethylaniline at the b. p. for thirty to forty-five minutes. 3:5-Dipropylsalicylic acid, needles, m. p. 100—100·5°, obtained by reducing 3:5-diallylsalicylic acid in alcoholic solution by the Paal-Skita method, is converted by boiling with dimethylaniline into 2:4-dipropylphenol, b. p. 263°/747 mm. or 130°/11 mm., D_{15}^{25} 0·9350 (*phenylcarbamate*, needles, m. p. 131°).

2:6-Diallylphenyl allyl ether, b. p. 132·5—134°/11 mm., D_{15}^{25} 0·9548, is prepared by heating an alcoholic solution of 2:6-diallylphenol with allyl bromide and potassium carbonate on the water-bath for ten hours. When it is heated in a current of carbon dioxide until the temperature rises from about 250° to about 290°, or, better, when it is boiled with half its weight of diethylaniline for fifteen minutes until the temperature rises from 225° to 248°, it is transformed into 2:4:6-triallylphenol (*loc. cit.*), b. p. 293—295°/760 mm. or 158—159°/14 mm., D_{15}^{25} 0·9785.

The influence of the b. p. of an allyl ether on the rapidity of its transformation into the allylphenol (*loc. cit.*) is well illustrated by the production of *o*-allylphenol, 2:6-diallylphenol, and 2:4:6-triallylphenol from the respective allyl ethers. The first reaction requires about six hours, the second proceeds much more rapidly, and the third almost instantly. It is to be noted, however, that the quantity of resinous matter produced is greater the higher is the temperature of transformation. The formation of this by-product is greatly diminished by heating in an atmosphere of hydrogen or carbon dioxide, or, best of all, by boiling the ether with dimethyl- or diethyl-aniline. The basic nature of this solvent appears to be of influence, since an indifferent, non-basic solvent of similar b. p. effects a much less satisfactory transformation.

cycloHexanol allyl ether, b. p. 169—172°/740 mm., D_{15}^{25} 0·8960, obtained by warming a benzene solution of cyclohexanol with sodium for one day and then boiling with allyl bromide, cannot be transformed into allylcyclohexanol.

II. Nitroso- and Amino-derivatives of Monoallylphenol and Diallylphenol [with F. KREMERS].—These two phenols yield nitroso-derivatives very smoothly. 4-Nitroso-2-allylphenol (2-allyl-p-benzoquinone-4-oxime), $\text{OH}\cdot\text{N}:\text{C}_6\text{H}_3(\text{C}_3\text{H}_5):\text{O}$, leaflets, m. p. 100—101° (decomp.), is obtained in the form of its sodium salt, garnet needles, by keeping a mixture of *o*-allylphenol, amyl nitrite, and concentrated methyl-alcoholic sodium methoxide solution for one day at the ordinary temperature and one day at 0°. The sodium salt, by warming on the water-bath for ten minutes with zinc dust and a cold, saturated solution of ammonium carbonate, or by treatment below 30° with hydrogen sulphide, a solution of ammonium chloride containing 25% aqueous ammonia being used as solvent,

is reduced to 4-amino-2-allylphenol, leaflets, m. p. 113·5—114°, the N-acetyl derivative of which forms leaflets, m. p. 93°.

4-Nitroso-2:6-diallylphenol (2:6-diallyl-p-benzoquinone-4-oxime), leaflets, m. p. 142—143°, obtained in a similar manner from 2:6-diallylphenol (a sodium salt is not precipitated in this case), yields 4-amino-2:6-diallylphenol, flattened prisms, m. p. 78·5°, by reduction with ammonium sulphide and concentrated aqueous ammonia.

III. *The Allyl Ether Transformation of Aminophenols* [with F. KREMERS].—*p*-Acetylaminophenol (used in preference to *p*-aminophenol to avoid allylation at the nitrogen atom) is boiled with acetone, allyl bromide, and potassium carbonate, and the resulting *p*-acetylaminophenyl allyl ether, leaflets, m. p. 93°, is boiled with dimethylaniline for six hours in a slow current of hydrogen, whereby the 4-acetyl-amino-*o*-allylphenol, m. p. 93°, described above is obtained; its ethyl ether, $\text{NHAc} \cdot \text{C}_6\text{H}_3(\text{C}_2\text{H}_5) \cdot \text{OEt}$, colourless leaflets, m. p. 121·5°, shows a very slight antipyretic action in comparison with phenacetin. By treatment with fuming hydrobromic acid, 4-acetyl-amino-*o*-allylphenol is converted into 4-acetyl-amino-1-methylcoumaran, $\text{NHAc} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{smallmatrix} \text{CHMe}$, colourless needles, m. p. 127—127·5°. By boiling for one hour with 10% hydrochloric acid or 25% sulphuric acid, *p*-acetylaminophenyl allyl ether is converted into the hydrochloride, leaflets, m. p. 212°, or the sulphate of *p*-aminophenyl allyl ether, both of which are very sparingly soluble in water. *p*-Aminophenyl allyl ether is converted into 4-amino-*o*-allylphenol (above) by heating with petroleum (b. p. 185°) for six hours in a current of hydrogen, and the latter into 4-amino-*o*-propenylphenol, $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH} \cdot \text{CHMe}$, silvery leaflets, m. p. about 172° (rapidly heated) or 168° (slowly heated), by boiling with very concentrated methyl-alcoholic potassium hydroxide in a slow current of hydrogen. The propenyl compound is more conveniently obtained by submitting 4-acetyl-amino-*o*-allylphenol to the same treatment.

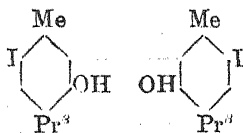
4-Acetyl-amino-*o*-allylphenol is converted by boiling acetone, allyl bromide, and potassium carbonate into 4-acetyl-amino-*o*-allylphenyl allyl ether, colourless leaflets, m. p. 111·5—112°, which yields 4-acetyl-amino-2:6-diallylphenol, leaflets and needles, m. p. 85—86°, by treatment by the dimethylaniline method; from the latter, 4-amino-2:6-diallylphenol (above) is obtained, but not satisfactorily, by boiling with dilute sulphuric acid in an atmosphere of hydrogen.

IV. *Synthesis of Eugenol* [with F. KREMERS].—Methyl guaiacol-carboxylate (3-methoxysalicylate), m. p. 66—66·5° (Fritsch gives 63°; Einhorn, 73°), is converted by boiling with methyl ethyl ketone, allyl bromide, potassium carbonate, and a little potassium iodide for seven hours into methyl 3-methoxy-2-allyloxybenzoate, b. p. 165—167°/8 mm., which yields the corresponding acid, $\text{C}_{11}\text{H}_{12}\text{O}_4$, needles, m. p. 65°, by hydrolysis with boiling 30% methyl-

alcoholic potassium hydroxide. When heated, the acid loses carbon dioxide and suffers transformation, yielding *o*-eugenol almost exclusively, but its methyl ester is converted almost explosively at 230—240° into *methyl 6-hydroxy-5-methoxy-3-allylbenzoate*, needles, m. p. 55—55·5°, b. p. 173—174°/12 mm. On account of the violence of the transformation, a method of heating under diminished pressure (in this case 200°/60 mm.) was tried, and gave such satisfactory results that it is recommended for the transformation of other allyl ethers into allylphenols. On hydrolysis, the preceding ester yields *6-hydroxy-5-methoxy-3-allylbenzoic acid*, prisms, m. p. 127° (hydrated, m. p. 85—88°), which is converted into eugenol by heating with dimethylaniline at 160°; the methyl ester also yields eugenol (and methylaniline) by boiling with aniline for four hours. C. S.

The Aristols and the Quantitative Estimation of Thymol.

E. MOLES and M. MARQUINA (*Anal. Fis. Quim.*, 1919, 17, 59—83).—Aristol is obtained⁸ as a red precipitate on adding a solution of iodine in potassium iodide to an alkaline solution of thymol (Messinger and Vortmann, A., 1889, 1150). On drying, the red substance loses water and iodine and passes into a yellow powder, one molecule of aristol giving 75 molecules of water and 0·15 atom of iodine. The freshly precipitated substance appears to behave as a gel in which iodine is adsorbed. The m. p. of both forms varies between 105° and 115°. A possible quinonoid or ketone structure was tested by means of hydriodic acid and by phenylhydrazine with negative results. Determinations of the molecular weight by cryoscopic measurements in benzene and thymol show that double molecules are present in the former solvent and single in the latter, the polymerisation indicating a phenolic structure. The constitution assigned to the yellow aristol is di-iododithymol (annexed formula). The following method for the estimation of thymol is given: The thymol, dissolved in water, is added to sodium hydrogen carbonate solution. A measured quantity of standard iodine solution in excess is added, and the mixture is acidified with sulphuric or hydrochloric acid. The excess of iodine is titrated with thiosulphate solution. Over wide ranges of variation in the value of the ratios thymol:sodium hydrogen carbonate and thymol:iodine added, the mean value of the quantity of iodine consumed was 3·60 atoms per molecule of thymol. W. S. M.

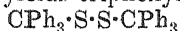


Triphenylmethyl Sulphur Compounds. D. VORLÄNDER and ERNST MITTAG (*Ber.*, 1919, 52, [B], 413—423. Compare A., 1913, i, 1335).—A poor yield of *triphenylmethyl sulphide*, $S(CPh_3)_2$, may be obtained by the interaction of triphenylchloromethane and alcoholic sodium sulphide or sodium triphenylmethyl sulphide, $CPh_3\cdot SNa$. It is a white powder, m. p. 182° (decomp.), which only

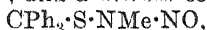
reacts with alcoholic mercuric cyanide on boiling, mercuric sulphide being formed.

When an ethereal solution of triphenylmethylthiol is treated in the cold with an equimolecular proportion of sulphuryl chloride, *triphenylmethyl thiocchloride* [*chlorothioltriphenylmethane*] is deposited in yellow prisms, m. p. 137°, according to the equation $\text{CPh}_3\cdot\text{SH} + \text{SO}_2\text{Cl}_2 = \text{CPh}_3\cdot\text{SCl} + \text{SO}_2 + \text{HCl}$. The compound is very stable towards water, but is decomposed by alkali hydroxides. The chlorine atom is readily replaced by other groups, using basic reagents, the following examples being described: (1) A solution of sodium methoxide gives *triphenylmethyl methoxyl sulphide*, $\text{CPh}_3\cdot\text{S}\cdot\text{OMe}$, needles, m. p. 124°, and sodium phenoxide forms *triphenylmethyl phenoxyl sulphide*, large prisms, m. p. 91·5°.

(2) Triphenylmethylthiol yields triphenylmethyl disulphide,



(*ibid.*). (3) Ammonia produces *triphenylmethyl sulphamide* [*triphenylmethylthiolamine*], $\text{CPh}_3\cdot\text{S}\cdot\text{NH}_2$, which crystallises in white rods, m. p. 126°, and forms an *acetyl* derivative, $\text{CPh}_3\cdot\text{S}\cdot\text{NHAc}$, needles, m. p. 187°, and a *benzylidene* compound, $\text{CPh}_3\cdot\text{S}\cdot\text{N}\cdot\text{CHPh}$, yellow needles, m. p. 128°. (4) Methylamine yields *triphenylmethyl methylsulphamide* [*triphenylmethylthiolmethylamine*], leaflets, m. p. 119—120°, which forms an *acetyl* derivative, prismatic needles, m. p. 133°, and a *nitroso*-compound,

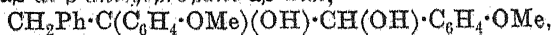


colourless crystals, m. p. 102—103° (decomp.). (5) Dimethylamine gives *triphenylmethylthiol dimethylamine*, m. p. 105—108°. (6) Aniline forms *triphenylmethyl phenylsulphamide* [*triphenylmethylthiolaniline*], white tablets, m. p. 103°, and *o*-toluidine gives *triphenylmethylthiol-o-toluidine*, leaflets, m. p. 141°.

If a solution of triphenylmethylthiol in benzene is shaken with sodium nitrite solution and gradually treated with dilute sulphuric acid, or slowly mixed with liquid nitrogen trioxide or peroxide, *triphenylmethyl thionitrite*, $\text{CPh}_3\cdot\text{S}\cdot\text{NO}$, separates in green needles, m. p. 104° (decomp.). Concentrated solutions of this ester in benzene appear red in transmitted light and green by reflected light. The thiol also couples with benzenediazonium chloride in the presence of sodium hydroxide, giving *triphenylmethylthiodiazobenzene*, $\text{CPh}_3\cdot\text{S}\cdot\text{N}_2\cdot\text{Ph}$, yellow leaflets, m. p. 108° (decomp.).

Chlorothioltrichloromethane (perchloromethyl mercaptan) condenses with benzene under the influence of aluminium chloride to form *thiobenzophenone*. Ph_3CS , a deep blue oil which yields benzophenone on boiling with alcoholic potassium hydroxide, and tetraphenylethylene on heating with copper powder. J. C. W.

Molecular Transpositions of the α -Glycols. V. The Dehydration of a Methoxy-derivative of $\alpha\beta\gamma$ -Triphenylpropane- $\alpha\beta$ -diol. A. ORÉKHOFF [with F. COMA y ROCA] (*Bull. Soc. chim.*, 1919, [iv], 25, 174—179. Compare this vol., i, 205, 206).—Magnesium benzyl bromide condenses with *p*-anisoin to give *γ -phenyl- $\alpha\beta$ -di-*p*-anisylpropane- $\alpha\beta$ -diol*,



m. p. 152—153°, which when dehydrated with sulphuric acid yields *benzyl-di-p-anisylacetaldehyde*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{CHO}$, m. p. 71—72°, giving an *oxime*, m. p. 116—118°. The aldehyde is decomposed by alcoholic potassium hydroxide, yielding α -*phenyl- β -di-p-anisylethane*, m. p. 89—90°. The constitution of this latter compound was proved by its synthesis as follows: Di-*p*-anisyl ketone condenses with magnesium benzyl chloride, giving *phenyl-di-p-anisylethyl alcohol*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{OH}$, m. p. 141—142°, which when dehydrated by acetyl chloride yields *phenyl-di-p-anisylethylene*, $\text{CHPh}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, m. p. 62—63°, and this, when reduced by sodium in absolute alcohol, gives α -*phenyl- β -di-p-anisylethane*.
W. G.

Molecular Transpositions of the α -Glycols. VI. Dehydration of $\alpha\beta\gamma$ -Tetraphenylpropane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVE] (*Bull. Soc. chim.*, 1919, [iv], 25, 179—182. Compare preceding abstract).—Magnesium benzyl chloride condenses with phenylbenzoin to give $\alpha\beta\gamma$ -*tetraphenylpropane- $\alpha\beta$ -diol*,
 $\text{OH}\cdot\text{CPh}_2\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\text{Ph}$,

m. p. 141—142°, which when dehydrated with sulphuric acid yields *benzyl triphenylmethyl ketone*, $\text{CPh}_3\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$, m. p. 113—113.5°; this is decomposed by alcoholic potassium hydroxide, giving triphenylmethane and potassium phenylacetate. W. G.

Molecular Transpositions of the α -Glycols. VII. The Dehydration of $\alpha\beta$ -Diphenylbutane- $\alpha\beta$ -diol and of $\alpha\beta$ -Diphenylmethylpentane- $\alpha\beta$ -diol. A. ORÉKHOFF [with J. ZIVE] (*Bull. Soc. chim.*, 1919, [iv], 25, 182—186. Compare preceding abstract).—By dehydrating $\alpha\beta$ -diphenylbutane- $\alpha\beta$ -diol with hot 20% sulphuric acid, Tiffeneau and Dorlencourt obtained $\alpha\alpha$ -diphenylbutaldehyde (compare A., 1906, i, 724). The authors, by using cold concentrated sulphuric acid, obtained ethyldeoxybenzoin and an *isomeride*, m. p. 32—33°, giving a *semicarbazone*, m. p. 191—192°, which was not characterised.

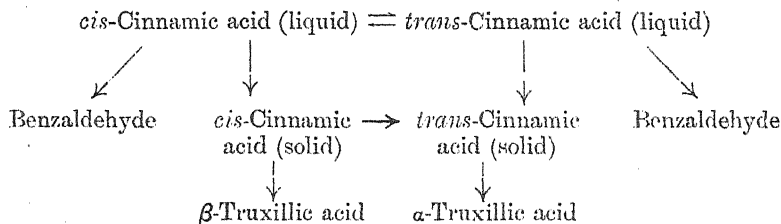
Magnesium isobutyl bromide condenses with benzoin to give $\alpha\beta$ -*diphenyl- δ -methylpentane- $\alpha\beta$ -diol*, m. p. 101—109°, which when dehydrated with cold concentrated sulphuric acid yields *isobutyldeoxybenzoin*.
W. G.

Molecular Transpositions of the α -Glycols. VIII. The Constitution of the Product of Dehydration of $\alpha\beta\beta$ -Triphenylethanedil. A. ORÉKHOFF (*Bull. Soc. chim.*, 1919, [iv], 25, 186—189).—The author agrees with Kohler (compare A., 1906, i, 753) that the product of dehydration of $\alpha\beta\beta$ -triphenylethanedil is diphenylacetophenone, $\text{CHPh}_2\cdot\text{COPh}$, and not the so-called triphenylvinyl alcohol, $\text{CPh}_2\cdot\text{CPh}\cdot\text{OH}$ (compare Biltz, A., 1899, i, 439). Diphenylacetophenone condenses with magnesium phenyl bromide to give $\alpha\alpha\beta\beta$ -*tetraphenylethyl alcohol*, m. p. 235—236°, which is also obtained by the action of magnesium phenyl bromide on diphenylacetyl chloride. The alcohol, when dehydrated, yields *tetraphenylethylene*.

Diphenylacetophenone condenses with magnesium benzyl chloride to give *ααβγ-tetraphenylpropan-β-ol*, m. p. 135—136°. W. G.

Action of Light on *allo*- and *iso*-Cinnamic Acids. HANS STOBBE (*Ber.*, 1919, 52, [B], 666—672).—Two specimens of cinnamic acid, m. p. 42°, obtained from the acids, m. p.'s 68° and 58° respectively, were exposed to bright daylight during two years; the product consisted entirely of unchanged acid and *β*-truxillic acid.

[With JUSSIK POGOSSIANZ.]—Specimens of cinnamic acids, m. p.'s 42°, 58°, and 68° respectively, were exposed in quartz tubes to direct sunlight which was sufficiently powerful in the circumstances to cause temporary fusion, with consequent isomerisation; in each case, the product consisted chiefly of *α*-truxillic acid with little *β*-truxillic acid and minimal quantities of *trans*-cinnamic acid and benzoic acid. Reaction in the illuminated molten mass, and also in benzene solution, may be represented by the scheme:



[With EDUARD FAERBER.]—The possible polymerisation of cinnamic acid by heat has been investigated either alone or in the presence of a solvent (water, naphthalene, xylene, ethylene dibromide). Polymerisation was only observed with certainty in the experiment with ethylene dibromide, when *α*-truxillic acid was formed in small amount. It is suggested that the action may be due to slight decomposition of the solvent into bromoethylene and hydrogen bromide, and the catalytic influence of the latter.

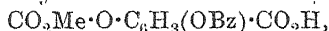
H. W.

The *O*-Benzoyl Derivatives of *β*-Resorcylic and Gentisic Acids. MAX BERGMANN and PAUL DANGSCHAT (*Ber.*, 1919, 52, [B], 371—388).—In a recent paper (*A.*, 1918, i, 172), Fischer described a remarkable reaction of the acyl derivatives of some aromatic acids containing at least two hydroxyl groups in neighbouring positions, namely, the wandering of an acyl group from one place to another during hydrolysis. For example, 4-benzoyl-3-acetylprotocatechuic acid yields 3-benzoylprotocatechuic acid. In order to prove whether this phenomenon is connected with the juxtaposition of the hydroxyl groups, Fischer has suggested the present investigation on *β*-resorcylic and gentisic acids, in which the hydroxyl groups are, respectively, in meta- and para-arrangement. The authors have succeeded in isolating the two pairs of

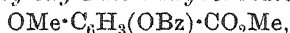
monobenzoates, but have found no indications of a tendency for the benzoyl group to wander from one position to the other.

Protocatechuic and gallic acids also only yield one carbomethoxy- or acetyl derivative, the acyl group being in the meta-position with respect to the carboxyl group. β -Resorcylic and gentisic acids yield *o*-acetoxy-compounds as well as meta- or para-derivatives.

2-Benzoyloxy-4-methylcarbonatobenzoic acid,



is obtained in long, thin needles, m. p. 148—149° (corr.), by the action of benzoyl chloride on carbomethoxyresorcylic acid (Fischer, A., 1909, i, 161), and is hydrolysed by means of *N*-ammonia solution to *4-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in concentric groups of needles, m. p. 160—161° (corr.). When treated with an excess of diazomethane in dry acetone, this acid yields *methyl 2-benzoyloxy-4-methoxybenzoate*,



which crystallises in needles or flat prisms, m. p. 69—70°, and is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to *4-methoxysalicylic acid*, m. p. 161° (corr.) (compare Tiemann and Parrisius, A., 1881, 270). The last compound affords the clue to the constitution of the benzoyloxy-acids.

2:4-Diacetoxybenzoic acid, well-developed, microscopic prisms, m. p. 136—138°, is obtained by heating β -resorcylic acid with acetic anhydride and zinc chloride, and is partly hydrolysed by dilute sodium hydroxide at 0° to *4-hydroxy-2-acetoxybenzoic acid*, which crystallises in lanceolate leaflets, m. p. 167—168° (corr.). This acid yields *methyl 2-acetoxy-4-methoxybenzoate*, m. p. 56—57°, on treatment with diazomethane, and this ester may be hydrolysed to *4-methoxysalicylic acid*. The acid also gives *4-benzoyloxy-2-acetoxybenzoic acid*, flat needles or prisms, m. p. 148—149° (corr.), when treated with benzoyl chloride and pyridine, and this is partly hydrolysed by a mixture of acetic and hydrochloric acids to *2-hydroxy-4-benzoyloxybenzoic acid*, needles, m. p. 193—194° (corr.). Treatment with diazomethane gives *methyl 4-benzoyloxy-2-methoxybenzoate*, m. p. 78—80°, which is hydrolysed by dilute aqueous-alcoholic sodium hydroxide to Fischer and Pfeffer's *4-hydroxy-2-methoxybenzoic acid*, decomp. 187—189° (corr.) (A., 1912, i, 559).

2-Benzoyloxy-5-methylcarbonatobenzoic acid, long, flat needles, m. p. 148—149° (corr.), is obtained from carbomethoxygentisic acid (A., 1909, i, 161) and hydrolysed by *N*-ammonia solution to *5-hydroxy-2-benzoyloxybenzoic acid*, which crystallises in microscopic leaflets, m. p. 211—212° (corr.). When treated with diazomethane, this yields *methyl 2-benzoyloxy-5-methoxybenzoic acid*, stout, quadratic plates, m. p. 106—107° (corr.), which gives the known *5-methoxysalicylic acid*, m. p. 145—146° (corr.), on hydrolysis (Tiemann and Müller, A., 1882, 52). A characteristic difference between this acid and the isomeric *5-hydroxy-2-methoxybenzoic acid*, m. p. 155—156° (Fischer and Pfeffer, *loc. cit.*), is that the

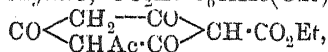
former gives a deep blue colour with ferric chloride and the latter only a grey colour.

5-Hydroxy-2-acetoxybenzoic acid, twinned prisms, m. p. 171—173° (corr.), is obtained by the partial hydrolysis of diacetyl-gentisic acid (Hemmelmeyer, A., 1909, i, 387) with *N*-ammonia in an atmosphere of hydrogen, and is converted by diazomethane into *methyl 2-acetoxy-5-methoxybenzoate*, m. p. 45—46°, which is hydrolysed to the above 5-methoxysalicylic acid. It is also converted into *5-benzoyloxy-2-acetoxybenzoic acid*, which crystallises in microscopic, bent needles, m. p. 166—167° (corr.), and yields *2-hydroxy-5-benzoyloxybenzoic acid*, leaflets, m. p. 178—179° (corr.), on hydrolysis with a mixture of acetic and hydrochloric acids. When treated with diazomethane, the acid gives *methyl 5-benzoyloxy-2-methoxybenzoate*, m. p. 83—84°, which may be hydrolysed to 5-hydroxy-2-methoxybenzoic acid. J. C. W.

Guaiaretic Acid. J. HERZIG and F. SCHIFF (*Ber.*, 1919, 52, [B], 260).—The authors agree with Schroeter and others (this vol., i, 84) that the formula of guaiaretic acid is $C_{20}H_{24}O_4$. J. C. W.

Some Derivatives of Phloroglucinol. ADOLF SONN (*Ber.*, 1919, 52, [B], 255—259).—Mosimann and Tambor have found that acetophloroglucinol will not condense with *p*-hydroxybenzaldehyde (A., 1916, i, 822), whereas its di- and tri-methyl ethers condense readily, and Sonn has found the same indifference in the case of ethyl acetophloroglucinolcarboxylate. This is most probably due to the fact that the compounds are really derivatives of triketo-hexamethylene.

The above ester is obtained by boiling a solution of Jerdan's lactone (A., 1917, i, 277; 1918, i, 33) in a mixture of acetic and hydrochloric acids, carbon dioxide being evolved. *Ethyl 2-acetylphloroglucinol-4-carboxylate*, $CO_2Et \cdot C_6HAc(OH)_3$ or



crystallises in bundles of slender needles, m. p. 77—78°, and changes into *ethyl phloroglucinolcarboxylate* when left with 25% potassium hydroxide. This ester crystallises from water with H_2O , or from alcohol in anhydrous prisms or needles, m. p. 129°.

When Jerdan's lactone is left for some time with 33% potassium hydroxide and the solution is acidified, *ethyl o-carboxyphloroacetophenonecarboxylate* [*3-carbethoxyphloroacetophenoneacetic acid*], $CO_2Et \cdot C_6H(OH)_3 \cdot CO \cdot CH_2 \cdot CO_2H$, is precipitated. The acid has m. p. 160°, and changes into the above ethyl 2-acetylphloroglucinol-4-carboxylate on melting or warming with acetic anhydride.

The silver salt of Jerdan's lactone, when heated with ethyl iodide, yields *ethyl 5:7-dihydroxy-4-ethoxy-1:2-benzopyrone-6(or 8)-carboxylate*, $CO_2Et \cdot C_6H(OH)_2 \begin{array}{c} O - CO \\ \diagup \quad \diagdown \\ C(OEt) \cdot CH \end{array}$, in thin, prismatic crystals, m. p. 160°.

J. C. W.

Constitution of Bile Acids. I. Cholanic, *iso*Cholanic, and ψ -Cholanic Acids. W. BORSCHÉ and EMMY ROSENKRANZ (*Ber.*, 1919, **52**, [B], 342—345).—When bilianic and *isobilianic* acids, $C_{19}H_{31}(CO)_2(CO_2H)_3$, are reduced by means of amalgamated zinc and hydrochloric acid, they yield cholanic and *isocholanic* acids, $C_{20}H_{33}(CO)(CO_2H)_3$. The ketone group of the latter pair of isomerides therefore corresponds in position with one ketone group of the former pair, and accordingly the $-CH\cdot OH-$ groups of deoxycholic acid and cholic acid which gave rise to these ketonic acids are identically placed. It has already been proved that the second alcoholic group of deoxycholic acid, $C_{24}H_{40}O_4$, is identical with a second group in cholic acid, $C_{24}H_{40}O_5$, the evidence being the great similarity between the ketonic tricarboxylic acids, namely, the pairs of bilianic and cholanic acids, which these hydroxy-acids yield on oxidation with permanganate. Consequently, cholic acid is a hydroxydeoxycholic acid.

When deoxycholic acid is oxidised by chromic acid, it yields dehydrodeoxycholic acid, $C_{21}H_{35}(CO)_2\cdot CO_2H$, and when this is oxidised by alkaline permanganate it gives ψ -cholanic acid, m. p. 259—260° (decomp.). This is another isomeride of cholanic acid, $CO\cdot C_{20}H_{33}(CO_2H)_3$, the constitution of which will be investigated more fully.

J. C. W.

Improved Preparation of Aromatic Aldehydes. GUSTAVE BLANC (Eng. Pat., 115244).—Aromatic aldehydes free from any trace of carboxylic acid are produced by boiling aromatic chloromethylene derivatives with an aqueous solution of an alkali dichromate, preferably with the addition of an alkali hydroxide or carbonate. The reaction is approximately represented by the equation $3R\cdot CH_2Cl + Cr_2O_7\cdot Na_2 + NaOH = 3NaCl + 3R\cdot CHO + Cr_2O_3 + 2H_2O$. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

G. F. M.

Terpenes and Ethereal Oils. CXXXVI. O. WALLACH (*Annalen*, 1919, **418**, 36—69).—I. *Conversion of Menthone into Pulegone* [with EMMA GROTE].—This work has already been recorded (*A.*, 1918, i, 544).

II. *Eucarvone Series* [with MAX STAUDACHER].—The experiments on the behaviour of halogenated cyclic ketones towards aqueous alkali (*A.*, 1918, i, 440, 442, 444) have been extended to include members of the eucarvone series. β -Dihydroeucarvone (*Annalen*, 1914, **403**, 91), the constitution of which has not yet been ascertained, is smoothly converted by bromine (1 mol.) in cold glacial acetic acid solution into a *dibromide*, $C_{10}H_{16}OBr_2$, prisms, m. p. 71—72°, which is isomeric with the dibromide, m. p. 68°, obtained by the bromination of tetrahydroeucarvone (*A.*, 1918, i, 444). The new dibromide, m. p. 71—72°, reacts rapidly with warm 2% aqueous potassium hydroxide, yielding volatile products and an *acid*, $C_{10}H_{16}O_2$. The volatile products have not been obtained in sufficient quantity for complete examination, but they consist chiefly of a ketone which shows no similarity to ketones of the

eucarvone series. It readily forms a *semicarbazone* ($? C_{11}H_{19}O_2N_3$ or $C_9H_{17}ON_3$), crystals, m. p. 194—195°, has an odour of camphor, behaves towards permanganate as an unsaturated compound, and by reduction with hydrogen and palladium yields a saturated ketone (*semicarbazone*, m. p. 196—197°).

The acid, $C_{10}H_{16}O_2$, is shown by direct comparison to be identical with Tiemann and Semmler's α -*cyclogeranic* (*isogeranic*) acid, m. p. 104—105°. Consequently, the dibromide, m. p. 71—72°, probably has the formula $\begin{array}{c} \text{CMe}_2 \cdot \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \end{array} > \text{CMeBr}$, and β -dihydroeucarvone has the 7-ring formula originally suggested (*loc. cit.*).

Since the dibromide contains a methylene group adjacent to a carbonyl group, it ought, according to previous experience of the bromination of cyclic ketones (*loc. cit.*), to undergo direct bromination. This is so. By treatment with bromine (1 mol.) in almost boiling glacial acetic acid, it yields a *tribromide*, $C_{10}H_{15}OBr_3$, m. p. 104—105°, which is only slowly attacked by 2% potassium hydroxide at 70°, yielding an *acid*, m. p. about 170°. The isomeric dibromide, m. p. 68°, obtained from tetrahydroeucarvone, does not undergo further bromination under the above conditions. The volatile products obtained when it is shaken with 2% alkali solution (*loc. cit.*) contain a small quantity of a hydrocarbon (?), b. p. 138—140°, and a yellow substance, b. p. 93—95°/8 mm., D_{20}^{20} 0.988, n_D^{20} 1.4813 (these values are only given provisionally), which does not yield any characteristic derivatives, but is converted by reduction with hydrogen and palladium into a *substance*, b. p. 223—225°, D_{20}^{20} 0.9690, n_D^{20} 1.4690 (*semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 212—213°; *oxime*, m. p. 55—56°), which is probably a cyclic ketone having its oxygen atom in a side-chain.

The acid, $C_{10}H_{16}O_2$, m. p. 91.5—92.5°, obtained by the action of 2% potassium hydroxide on dibromotetrahydroeucarvone (*loc. cit.*), is converted by oxidation with alkaline permanganate into a mixture of three acids, $C_{10}H_{16}O_3$, m. p. 159—160°, $C_{10}H_{14}O_3$, m. p. 187°, the third acid, m. p. 90—91°, being produced in very small quantity.

Since the preceding brominated 7-ring ketones of the eucarvone series differ from halogenated 6-ring ketones in yielding volatile products as well as an acid by treatment with 2% potassium hydroxide, *dibromosuberone*, $C_7H_{10}OBr_2$, m. p. 70—72°, has been shaken with dilute potassium hydroxide solution at 70°, whereby a volatile ketone (*semicarbazone*, m. p. 190—191°) and an acid, probably tetrahydrobenzoic acid, have been obtained. C. S.

Adsorption of the Glucosides of Digitalis Leaves. C. MANNICH (*Ber. Deut. pharm. Ges.*, 1919, 29, 206—213).—Experiments with gitalin showed the latter to be readily adsorbed from aqueous solution by blood charcoal (the latter can adsorb at least 20% of its weight), less readily from alcoholic solution, and still less readily from solution in chloroform. A specimen of charcoal containing 20% of gitalin did not lose glucoside when treated with

water, and only a portion when alcohol was used, but practically all of it was removed by chloroform. Other substances, such as fuller's earth, the sulphides of lead, copper, or zinc, and particularly those of arsenic and antimony, have the power of adsorbing the bitter principles from an aqueous extract of *digitalis* leaves. Attempts to isolate the glucosides by treatment of infusion of *digitalis* with animal charcoal and subsequent extraction of the latter with chloroform did not lead to the desired result, possibly because the principles are not free in the aqueous solution, but in complex compounds with other substances, such as tannins.

The author considers that the readiness with which the *digitalis* glucosides are adsorbed by the powdered drug explains the difficulty of their complete extraction, and also the better results which are obtained when water, as solvent, is replaced by alcohol. H. W.

Syntheses of Depsides, Lichen Substances, and Tannins.

II. EMIL FISCHER (*Ber.*, 1919, 52, [B], 809—829).—A general résumé of the progress made by Fischer and his co-workers in this field since the year 1913; the individual subjects have been previously abstracted. H. W.

Tannin and the Synthesis of Similar Substances. VI.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1919, 52, [B], 829—854. Compare A., 1912, i, 471, 887; 1913, i, 479; 1915, i, 437; 1918, i, 87).—The removal of acetyl groups from substances such as the acetates of galloyl- and digalloyl-glucose, previously effected with cold alkali or with warm sodium acetate solution, can also be effected at the ordinary temperature by a moderate amount of concentrated aqueous hydrochloric acid in methyl-alcoholic solution. If the acetyl derivative is too sparingly soluble in methyl alcohol, a mixture of the latter with acetone may be used. The penta(*m*-digalloyl)- α - and - β -glucoses obtained in this manner from the acetates are optically purer than those previously obtained. The method can also be applied with good results to simpler substances, such as acetylsalicylic acid and triacetyl gallic acid.

The use of the potassium salt for the purification of tannins was recommended by Berzelius. The authors find the most convenient method of preparation to consist in mixing alcoholic solutions of the natural or synthetic tannins and potassium acetate, but the precipitates contain small quantities of the latter. The salts from Chinese tannin, pentadigalloyl- α -glucose, pentadigalloyl- β -glucose, and pentagalloyl glucose have $[\alpha]_D^{20} +46.3^\circ$, $+56.6^\circ$, and $+33.7^\circ$, respectively, in water. The salt appears to be suitable for the separation of artificial tannins from many other substances and for their purification, but not suitable for the differentiation of the individual galloyl glucoses.

Attempts have been made to extend the method used in the preparation of 1-monogalloyl- β -glucose (this vol., i, 89) to other 1-acylglucoses, but the results are disappointing, as frequently the acyl group is removed simultaneously with the acetyl groups. This

is, for example, the case with *1-benzoyltetra-acetyl- α -glucose*, long, colourless needles, m. p. 60—63°, but frequently several degrees lower, owing possibly to dimorphism, $[\alpha]_D^{25} + 113.5^\circ$ in chloroform. On the other hand, *1-p-acetoxylbenzoyltetra-acetyl- β -glucose*, colourless needles, m. p. 172—173° (corr.), $[\alpha]_D^{25} - 30.6^\circ$ in *s*-tetrachloroethane, could be converted by alcoholic sodium hydroxide or alcoholic ammonia into *1-p-hydroxylbenzoyl- β -glucose*, flat needles, m. p. about 228° (corr.; decomp.) when rapidly heated, $[\alpha]_D^{25} - 23.9^\circ$ in *s*-tetrachloroethane; in the latter case, *1-p-hydroxylbenzoyltetra-acetyl- β -glucose*, m. p. 196—197° (corr.), $[\alpha]_D^{25} - 38.4^\circ$ in acetone, is formed as intermediate product. Similarly, *1-p-acetoxylbenzoyltetra-acetyl- α -glucose*, m. p. 134—135° (corr.), $[\alpha]_D^{25} + 116^\circ$ in *s*-tetrachloroethane, could be de-acetylated with alcoholic sodium hydroxide, but the product was a syrup which could not be caused to crystallise or reconverted into the pure penta-acetate.

The catalytic action of sodium alkylxide on esters in alcoholic solution has been applied for the removal of acetyl groups. Thus, for the elimination of the five acetyl groups of *p*-acetoxybenzoyltetra-acetylglucose dissolved in alcohol, one molecule of sodium ethoxide is sufficient at the ordinary temperature, and the presence of a small quantity of water in the alcohol does not hinder the reaction; these conditions are particularly advantageous for securing good yields. The method has also been applied to the isolation of dextrose from its penta-acetate and of α -methylglucoside from its tetra-acetate.

Attempts to prepare 1-galloyl- α -glucose are described. It is found that the specific rotation of 1-galloyl- β -glucose gradually changes from negative to positive, and finally attains a maximum when its aqueous solution is agitated with calcium carbonate, or, more rapidly, with sodium carbonate or pyridine; in all probability, the change in sign is caused by the conversion of 1-galloyl- β -glucose into the α -derivative, but attempts to isolate the latter from the product were not successful. Crude tetra-acetyl- α -glucose, obtained by inversion of the β -compound, was therefore treated with triacetylgalloyl chloride in the presence of quinoline, whereby ultimately *triacetylgalloyltetra-acetyl- α -glucose*, microscopic needles, m. p. 158—159° (corr.), $[\alpha]_D^{25} + 99.9^\circ$ in *s*-tetrachloroethane, was isolated; this was then hydrolysed with alcoholic ammonia, but the product was not crystalline. It appeared, however, to contain considerable amounts of 1-galloyl- α -glucose, since, on re-acetylation, it yielded the hepta-acetyl derivative in quantity.

The galloyl derivatives of the sugars differ among themselves in their behaviour towards gelatin solutions. The penta- and tri-galloyl compounds precipitate the latter from aqueous solution in the same manner as do the tannins, but this property is not shown by the varying monogalloyl glucoses nor by monogalloyl fructose. Since similar differences were to be expected among the poly-hydroxy-alcohols, the derivatives of glycol, trimethyleneglycol, glycerol, erythritol, and mannitol have been prepared and ex-

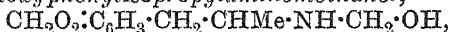
aminated. They are readily obtained from the alcohols by coupling with triacetylalloyl chloride and subsequent removal of the acetyl groups. The crystalline *ethyleneglycol digallate* is so sparingly soluble in water or alcohol that its reaction with gelatin and arsenic acid cannot be investigated. With *trimethyleneglycol digallate*, the gelatin test is not characteristic, but distinct gelatinisation is caused by arsenic acid in alcoholic solution. *Erythritol tetragallate* is readily soluble in water and coagulates gelatin, but the alcoholic solution is too dilute to be tested with arsenic acid. The amorphous *glyceryl trigallate* and *mannitol hexagallate* yield colloidal solutions in water and behave like tannins towards both reagents. The physical properties of this series of substances are as follows: *ethyleneglycol ditriacetyl-gallate*, colourless leaflets, m. p. 172—173° (corr.) after slight softening; *ethyleneglycol digallate*, microscopic needles, which decompose at about 287° (corr.) without melting; *glyceryl tri-triacetyl-gallate*, amorphous powder; *glyceryl trigallate*, pale yellow, amorphous, brittle mass. [With (FRL.) HERTHA VON PELCHERZIM.]—*Trimethyleneglycol ditriacetyl-gallate*, leaflets, m. p. 159—160°; *trimethyleneglycol digallate*, leaflets, m. p. about 270° (decomp.); *erythritol tetra-triacetyl-gallate*, small, colourless needles without definite m. p.; *erythritol tetragallate*, which when rapidly heated darkens at about 288°, and is completely decomposed at about 308°; *mannitol hexa-triacetyl-gallate*, amorphous, pale brown substance; *mannitol hexagallate*, amorphous, pale brown substance, $[\alpha]_D^{25} + 27.0^\circ$ in alcohol.

H. W.

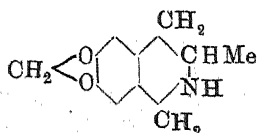
The Resolution of Hyoscine and its Components, Tropic Acid and Oscine. HAROLD KING (T., 1919, 115, 476—508).

A New Synthesis of Hydrastinine and its Homologues. KARL W. ROSENMUND (*Ber. Deut. pharm. Ges.*, 1919, 29, 200—206).—Starting from methylenedioxyphenylisopropylamine, the synthesis of certain homologues of hydrastinine has been effected, whilst the alkaloid itself has been prepared from homopiperonylamine by a new method.

Methylenedioxyphenylisopropylaminomethanol,



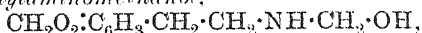
is obtained as a viscous, colourless, somewhat unstable oil by the action of chloromethyl alcohol on methylenedioxyphenylisopropylamine in dry ethereal solution, and is converted by warming with 10% aqueous hydrochloric acid into 3-methyldihydronorhydrastinine hydrochloride, m. p. 231—232°; the free base (annexed formula) crystallises in colourless leaflets, m. p. 57—58°; the *hydriodide* forms colourless leaflets, m. p. 215—217°. Methylation of the base, preferably with formaldehyde, gives 3-methyldihydrohydrastinine, m. p. 85—87° (*hydrochloride*, m. p. 230—232°; *hydriodide*, m. p. 240°; *perchlorate*, colour-



less needles, m. p. 215°), which can also be prepared from methylenedioxyphenylisopropylmethylamine. Oxidation with potassium dichromate and sulphuric acid or with iodine leads to the formation of 3-methylhydrastinine, m. p. 107—108° (*hydriodide*, yellow leaflets, m. p. 210—212°; *perchlorate*, greenish-yellow needles, m. p. 212°).

Phenylacetylmethylenedioxyphenylisopropylamine, colourless needles, m. p. 105—106°, is prepared by the action of phenylacetyl chloride on the amine, and is converted by treatment with phosphoric oxide into 1-benzyl-3-methylnorhydrastinine, yellow syrup (*picrate*, m. p. 182°; *hydriodide*, shining prisms, m. p. 208°).

Homopiperonylaminomethanol.



is obtained as a colourless, very unstable oil by the action of chloromethyl alcohol (1 mol.) on homopiperonylamine (2 mols.) in ethereal solution, and is converted by 10% aqueous hydrochloric acid into dihydronorhydrastinine, identical with the product described by Decker (A., 1911, i, 906).

H. W.

Porphyroxine. JITENDRA NATH RAKSHIT (T., 1919, 115, 455—461).

Syntheses in the Indole Series. Homologues of Di-oxindole and Isatin. J. MARTINET (*Ann. Chim.*, 1919, [ix], 11, 15—84, 85—130).—For the most part a more detailed account of work already published (compare A., 1913, i, 756; 1918, i, 306, 345, 351). The following new compounds are described.

Methyl diacetyl-5-methyldioxindole-3-carboxylate, m. p. 132°, and the corresponding *ethyl* ester, m. p. 110°.

Methyl 5:7-dimethyldioxindole-3-carboxylate, m. p. 260°, and its *diacetyl* derivative, m. p. 227°; the corresponding *ethyl* ester, m. p. 215°, and its *diacetyl* derivative, m. p. 203—204°; 5:7-dimethyldioxindole, m. p. 228—229°, and its *O-acetyl* derivative, m. p. 201—202°.

Methyl acetyl-1-methyldioxindole-3-carboxylate, m. p. 146°, and the *ethyl* ester, m. p. 65°.

Ethyl 5-bromo-1-methyldioxindole-3-carboxylate, m. p. 160°, and its *acetyl* derivative, m. p. 132°; 5-bromo-1-methyldioxindole, m. p. 162°, and its *O-acetyl* derivative, m. p. 115°; 5-bromo-1-methylisatinphenylhydrazone, m. p. 164°.

Ethyl acetyl-1-ethyldioxindole-3-carboxylate, m. p. 68°.

Ethyl 5-bromo-1-ethyldioxindole-3-carboxylate, m. p. 106°, and its *acetyl* derivative, m. p. 120°; 5-bromo-1-ethylisatin, m. p. 144°, and its *phenylhydrazone*, m. p. 124°.

Methyl 3-hydroxy-2-keto-1-ethyldihydro-ββ-naphthindole-3-carboxylate, m. p. 203°, and its *acetyl* derivative, m. p. 140°, and the *acetyl* derivative, m. p. 114°, of the corresponding *ethyl* ester.

Ethyl 3-acetyl-1:7-trimethylenedioxyindole-3-carboxylate, m. p. 95°.

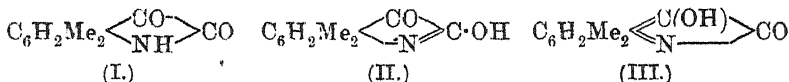
5-Methyl-1:7-trimethylenedioindole, m. p. 193°; 5-methylisatin-phenylhydrazone, m. p. 268°; 1-ethylisatinphenylhydrazone, m. p. 74°; N-ethyl-β-naphthisatinphenylhydrazone, m. p. 180°.

β-Naphthisatoic acid (β-amino-α-naphthylglyoxylic acid) is very unstable, but gives potassium, copper, lead, and silver salts.

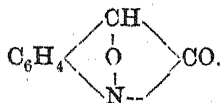
5-Bromo-N-methylisatoic acid (5-bromo-2-methylaminophenylglyoxylic acid) is very unstable, but gives potassium, copper, silver, and lead salts; 5-bromo-N-ethylisatoic acid also gives potassium, copper, silver, and lead salts.

N-Ethyl-β-naphthisatoic acid (β-ethylamino-α-naphthylglyoxylic acid) gives potassium, copper, and lead salts. W. G.

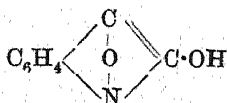
New Isomerides in the Isatin Series. III. GUSTAV HELLER (*Ber.*, 1919, **52**, [B]. 437—446. Compare A., 1917, i, 219; 1918, i, 235; this vol., i. 36).—The constitutions of three of the four modifications of 5:7-dimethylisatin have already been established, and the following formulæ assigned to them:



In the case of isatin itself, only the isomerides corresponding with these three formulæ have been established so far, but it is now found that when the methyl ether of the lactim form (II) of isatin is heated with benzene at 200—205°, it is partly converted into the N-methyl ether of the lactam form (I) and partly demethylated and transformed into a new isomeride which corresponds with the fourth modification of dimethylisatin. This is a feeble base the salts of which are hydrolysed by water. It does not react with diazomethane, methyl iodide, sodium hydrogen sulphite, or Fehling's solution, neither does it form an acetyl or benzoyl derivative nor give the indophenine reaction. It is more soluble in benzene than the other product, and its properties are best expressed in the annexed formula. The compound is designated *isatinone*, and it crystallises in well-developed, dark honey-coloured, quadratic prisms, m. p. 226° (decomp.). It dissolves slowly in 0.5N-sodium hydroxide, and if the solution is quickly precipitated by



50% acetic acid, a fifth isomeride, *isatinol* (annexed formula), is obtained in orange-yellow flocks, m. p. 255°, which reverts to isatinone on crystallisation from glacial acetic acid or benzene. The methyl ether of the fourth modification of dimethylisatin should conform to the same type. If the red solution in sodium hydroxide is exposed to light, however, it becomes pale in time and deposits



Friedländer and Roschdestwensky's anhydro-α-isatinanthranilide, $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} \\ \diagdown \text{O} \\ \diagup \text{N} \end{array} \text{C}\cdot\text{OH}$ (A., 1916, i, 80).

If the methyl ether of the lactim form of isatin is heated with methyl alcohol at 200° instead of with benzene, it yields this anhydro- α -isatinanthranilide and a *hydrate* of it, $C_{15}H_{10}O_3N_2$, colourless crystals, m. p. 172°, which yields anthranoylanthranilic acid when boiled with alcoholic potassium hydroxide.

J. C. W.

An Improved Method of Preparing Indican from Indigo-yielding Plants. BHAILAL M. AMIN (*Agric. Res. Inst. Pusa, Indigo Publ.* No. 5).—The method, which is far more rapid than any of the methods hitherto described, consists in extracting the fresh leaf with hot water so as to dissolve the indican. Freshly slaked lime is added to the extract to precipitate impurities, such as amino-acids, tannins, gums, etc. The purified liquor is filtered, evaporated, and the indican extracted from the concentrated solution with acetone. The wet extract is evaporated to remove the acetone, and on cooling in ice the aqueous solution which is left, indican hydrate separates. The crude hydrate is purified by dissolving it in absolute alcohol and precipitating with benzene, when pure anhydrous indican crystallises. This method gives an excellent yield (70–80%), and can be applied to any species of plant, and by its use pure indican has, for the first time, been prepared in large quantities from Java indigo (*Indigofera arrecta*).

W. G.

New Transitions from the Indole to the Quinoline Series. GUSTAV HELLER (*Ber.*, 1919, 52, [B], 741–745).—It has been previously shown (Heller and Wunderlich, A., 1914, i, 865) that 2-cyano-2:3-dihydroindole-2-carboxylamide is converted by nitrous fumes into 2-hydroxyquinoline-3-carboxylamide. A similar conversion of the 5-membered to the 6-membered ring occurs when diazomethane acts on an ethereal suspension of isatin, 2:3-dihydroxyquinoline, needles, m. p. 190–192°, being obtained (compare Madelung, A., 1913, i, 91). The latter, with more diazomethane, appears to yield a monomethyl ether; with acetic anhydride, it gives a monoacetyl derivative, long needles, m. p. 214–215°.

Under similar conditions, *dihydroxy-6:8-dimethylquinoline*, m. p. about 242° (decomp.), is obtained from 2:4-dimethylisatin lactam, whilst 2:4-dimethylisatin lactim yields a *product*, aggregates of needles, m. p. 253° (decomp.).

Dimethylisatol and dimethylisatinone are normally alkylated by diazomethane, yielding, however, different substances, which are insoluble in alkali. Oxindole, dioxindole, and phthalimidine are not attacked by ethereal solutions of diazomethane.

H. W.

Action of Organomagnesium Compounds on Quinoline Methiodide. Stereochemistry of Compounds of Nitrogen. MARTIN FREUND and ELISABETH KESSLER (*J. pr. Chem.*, 1918, [ii], 98, 233–254. Compare A., 1905, i, 156; 1909, i, 417).—The action of magnesium propyl bromide on quinoline

methiodide yields 1-methyl-2-propyldihydroquinoline, $C_{13}H_{17}N$, as a golden-yellow, unstable oil, b. p. 268—270° (compare von Braun and Aust, A., 1915, i, 586); the *picrate* forms needles, m. p. 157—158°. The base combines with methyl iodide, yielding a crystalline *methiodide*, m. p. 158—160° (decomp.), which is converted at its melting point or by crystallisation from dilute alcohol into a compound, $C_{13}H_{16}NI$, m. p. 184°, which is identified as 2-propylquinoline methiodide. 1 : 2-Dimethyl-1 : 2-dihydroquinoline methiodide, yellowish-red crystals, m. p. 212—213°, does not exhibit similar behaviour. The dihydro-base does not yield crystalline salts; it combines with bromine, yielding a *perbromide*, $C_{13}H_{17}NBr_4$, needles, m. p. 158°, which, when treated with sulphurous acid and subsequently with sodium iodide, gives 3(4)-bromo-1-methyl-2-propyl-1 : 2-dihydroquinoline hydriodide, a yellow, crystalline salt, m. p. 242°, after darkening at 235°. The base is reduced by tin and hydrochloric acid to 1-methyl-2-propyltetrahydroquinoline, b. p. 270—280° (compare von Braun and Aust, *loc. cit.*), which, when obtained in this manner, appears to be a mixture of two bases, one of which has b. p. 274—278° and forms a crystalline *hydrochloride*, long needles, m. p. 237—238°, *hydrobromide*, needles, m. p. 223—224°, and *hydriodide*, m. p. 176° after softening at 168°, but does not give a crystalline methiodide, whilst the other, b. p. 272—276°, does not yield crystalline salts, but forms a crystalline *methiodide*, colourless leaflets, m. p. 196—197° after some decomposition at 190°.

The action of magnesium *isobutyl iodide* on quinoline methiodide has been similarly studied with the object of discovering further instances of stereoisomerism of similar character. 1-Methyl-2-isobutyldihydroquinoline forms an unstable oil, b. p. 278—280° (*picrate*, shining needles, m. p. 154—155°; the *methiodide* is not crystalline), which, as in the case of the propyl compound, is reduced to a mixture of bases, b. p. 260—280°, separable by means of their hydrochlorides. The one of these is a pale yellow, almost odourless oil, b. p. 283° (*hydrochloride*, transparent needles, m. p. 223—224°; *hydrobromide*, m. p. 225° after previous softening; *hydriodide*, m. p. 183—184°; *methiodide*, m. p. 168°), whilst the other is darker in colour, less pleasant in odour, has b. p. 263°, forms readily soluble salts with the halogen acids, and gives a *methiodide*, m. p. 174° after previous softening.

1-Methyl-2-isopropyldihydroquinoline is a yellow, unstable oil, b. p. 268—274° (*picrate*, needles, m. p. 184°); it is reduced by tin and hydrochloric acid to 1-methyl-2-isopryltetrahydroquinoline, b. p. 265—266°. In this instance, the separation of possible isomerides could not be effected by means of halogen acids, owing to the solubility of the salts formed. Probably a mixture of stereoisomerides is present, since the crystalline *methiodide* (yellow needles, m. p. 179—180°) isolated from the crude base does not correspond in quantity with the weight of base used.

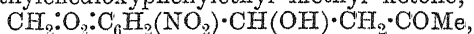
2-Benzyl-1-methyldihydroquinoline is obtained in poor yield by

the action of magnesium benzyl chloride on quinoline methiodide; the crude product is separable into two fractions, b. p. 125—140°/13—20 mm. and 140—155°/13—20 mm. respectively.

3-Bromo-2-phenyl-1-methyldihydroquinoline, b. p. 270°/75 mm., forms a brown, feebly basic oil, which has only a slight tendency towards salt formation; the *picrate* crystallises in four-sided leaflets, m. p. 185° after softening at 175°. H. W.

Some Derivatives of 6:7-Dihydroxyquinoline. W. BORSCHKE and R. QUAST (*Ber.*, 1919, 52, [B], 432—437).—A good method for the preparation of Haber's 6:7-methylenedioxy-2-methylquinoline is described (compare A., 1891, 705).

Piperonaldehyde is nitrated, and the 6-nitro-derivative, which is formed in good yield, is condensed with acetone in the presence of 3% potassium carbonate, whereby a 75% yield of β -hydroxy- β -6-nitro-3:4-methylenedioxyphenylethyl methyl ketone,



is obtained (compare Herz, A., 1905, i, 778). This is reduced by means of zinc dust in a mixture of acetic and hydrochloric acids, an excellent yield of 6:7-methylenedioxy-2-methylquinoline being obtained. The base has m. p. 150°, b. p. 306—308°/743 mm., and forms a *methiodide*, m. p. 277—278°, and a *methochloride*, m. p. 265—266°, which gives a *double salt* with mercuric chloride, m. p. 193° (decomp.). It condenses with benzaldehyde under the influence of zinc chloride to form 2-styryl-6:7-methylenedioxyquinoline, m. p. 179—180°, and it suffers reduction by sodium and alcohol to 6:7-methylenedioxy-2-methyl-1:2:3:4-tetrahydro-

quinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{NH}-\text{CHMe} \end{matrix}$. This is a snow-white base, m. p. 44—45°, which forms a *nitroso-compound*, yellow needles, m. p. 85—86°, and a *methiodide*, m. p. 176—177°.

The corresponding phenylquinoline has also been prepared. Piperonylideneacetophenone is nitrated, and the phenyl 2-nitro-4:5-methylenedioxy-styryl ketone so formed, which crystallises in flat, yellow needles, m. p. 165—166°, is reduced by zinc dust and a mixture of acetic and hydrochloric acids. 6:7-Methylenedioxy-

2-phenylquinoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2\begin{matrix} \text{CH}\cdot\text{CH} \\ \text{N}=\text{CPh} \end{matrix}$, crystallises in very pale yellow leaflets, m. p. 110°, and its *picrate* has m. p. 192°.

J. C. W.

ψ -1:8-isoNaphthoxazones. BIMAN BIHARI DEY and MAHENDRA NATH GOSWAMI (*T.*, 1919, 115, 531—541).

The Asymmetric Nitrogen Atom. LI. Abnormal Quaternary Ammonium Salts. E. WEDEKIND and TH. GOOST (*Ber.*, 1919, 52, [B], 446—459).—In the last communication (A., 1916, i, 671), a diquaternary ammonium salt was described having two asymmetric nitrogen atoms of unlike asymmetry, namely, the

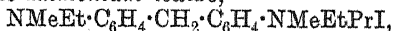
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salt of the formula $\text{NMePh}(\text{C}_7\text{H}_7)\text{Br}\cdot\text{C}_3\text{H}_6\cdot\text{NMePh}(\text{C}_3\text{H}_5)\text{I}$. With the hope of obtaining similar salts, experiments have been conducted with *pp'*-dimethyldiethyldiaminodiphenylmethane. When this is treated with one molecular proportion of benzyl bromide or allyl iodide, normal addition takes place (Fröhlich, A., 1911, i, 493), but *sec*-butyl iodide does not react, and propyl bromide or iodide, and *isobutyl* and ethyl iodides give abnormal products of the type $2[\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMeEt})_2]\cdot\text{RX}$.

The abnormal propiodide has been studied most completely. Attempts to convert it into the corresponding chloride, bromide, nitrate, or camphorsulphonate give rise to the free ditertiary base and the normal amino-ammonium salt, which can be precipitated as the normal iodide on the addition of potassium iodide. Silver oxide gives the same result. By treatment with silver perchlorate, however, an abnormal perchlorate may be obtained. The salt is also decomposed into the base and normal iodide by the action of aqueous-alcoholic ammonia, and benzyl bromide reacts in a manner which is to be interpreted in the same way.

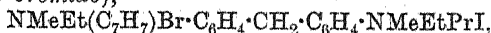
The normal iodide combines with the base to form the abnormal salt, and reacts with benzyl bromide to form a salt with two unlike asymmetric nitrogen atoms of the desired type. Attempts to resolve this into the expected four optical isomerides gave no definite results.

The "*abnormal propiodide*," $(\text{C}_{19}\text{H}_{26}\text{N}_2)_2\cdot\text{C}_3\text{H}_7\text{I}$, is best obtained by heating equimolecular proportions of the base (Fröhlich, *ibid.*) and propyl iodide at 100° in a sealed tube. It crystallises from methyl alcohol with m. p. 153° , and its solutions become deep blue on exposure to the air. The abnormal perchlorate has m. p. $133\cdot5^\circ$. The normal iodide, *methylethylpropyl-methylethylamino-diphenylmethane-ammonium iodide*,



has m. p. $158\cdot5^\circ$, the corresponding *nitrate* has m. p. $155\cdot5^\circ$, and the first crystals of the *d-camphorsulphonate* have $[\text{M}]_D + 59\cdot72^\circ$, which is about the same as that of the anion itself.

Diphenylmethanediammonium-(methylethylpropyl iodide)-(methylethylbenzyl bromide),



obtained by the action of benzyl bromide on the normal iodide, is separated by alcohol into a sparingly soluble fraction, decomp. about 175° , and a semi-solid portion. The *di-iodide* corresponding with the first fraction has m. p. 187° , and the *diperchlorate*, m. p. 225° , whilst the salts of the second portion have m. p.'s 182° and 222° respectively. The mixture of diperchlorates has m. p. 221° , and can be isolated from the product of the action of benzyl bromide on the abnormal iodide.

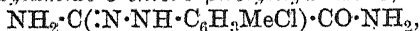
The base also forms an "*abnormal ethiodide*," m. p. $144\text{--}145^\circ$, and "*abnormal isobutiodide*," m. p. $140\text{--}141^\circ$, but methyl iodide converts it into *diphenylmethane-pp'-bisdimethylethylammonium di-iodide*, $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{EtI})_2$, colourless needles, m. p. 203° .

J. C. W.

I. Syntheses and Reactions of New Monoaryl-hydrazidine Carboxylic Esters. II. Oxidative Fission by means of Chlorine of Organic Substances containing the Hydrazone and Hydrazidrazone Groups. (I.) CARL BÜLOW and RICH. ENGLER. (II.) CARL BÜLOW (*Ber.*, 1919, **52**, [B], 632—651).—In continuation of the work of Bülow and Engler (this vol., i, 47), the authors have now prepared ethyl α -aminoglyoxylate 3-chloro-*p*-tolylhydrazone, the corresponding amide and hydrazide, and have made an extended study of their reactions. They are led to the following general conclusions: Benzaldehyde arylhydrazones and their derivatives are primarily converted into pure chlorinated products by treatment with chlorine in a suitable solvent; as secondary change, the hydrazone is converted into the corresponding diazonium or chloroaryldiazonium group. The arylhydrazone residue is eliminated from hydrazidines or amidrazones as diazonium salt by the agency of chlorine. Nitrogen is eliminated by chlorine from acid hydrazidrazones and azines, but the fate of the remainder of the molecule has not yet been elucidated.

*Ethyl α -aminoglyoxylate-3-chloro-*p*-tolylhydrazone* is obtained as colourless, shining leaflets, m. p. 86° , by the action of alcoholic ammonia at the ordinary temperature on ethyl α -chloroglyoxylate-3-chloro-*p*-tolylhydrazone. The *hydrochloride* has m. p. 173 — 174° . The ester is readily decomposed by chlorine in acetic acid solution, and the diazonium salt of 3-chloro-*p*-toluidine which is produced is readily identified by coupling it with β -naphthol, the *product* forming long, red needles, m. p. 179 — 179.5° . Boiling concentrated aqueous hydrochloric acid decomposes the ester, yielding ammonium chloride, oxalic acid, and 3-chloro-*p*-tolylhydrazine hydrochloride; on account of its instability, the free base was not investigated. It reacts with *m*-nitrobenzaldehyde to yield *m*-nitrobenzaldehyde-3-chloro-*p*-tolylhydrazone, m. p. 175° , which is decomposed by nitric acid with production of a diazonium salt; this, with chlorine in acetic acid solution, gives the *substance*, $C_{14}H_{12}O_2N_3Cl$, long, yellow needles, m. p. 139° . 2:5-Dichlorobenzaldehyde-3-chloro-*p*-tolylhydrazone, slender needles, has m. p. 108° , and also yields a diazonium salt when treated with concentrated nitric acid, and a *substance*, m. p. 114 — 115° , when acted on by chlorine. The constitution of the hydrazine is definitely decided by preparation of the condensation products with *m*-nitrobenzaldehyde and 2:5-dichlorobenzaldehyde from synthetic 3-chloro-*p*-tolylhydrazine, and the identity of the products thus obtained with those previously prepared.

*α -Aminoglyoxylamide-3-chloro-*p*-tolylhydrazone,*



thick, greyish-white needles, m. p. 170 — 171° , is prepared by the more protracted action of alcoholic ammonia on ethyl α -chloroglyoxylate 3-chloro-*p*-tolylhydrazone; it is completely decomposed by nitric acid, and is quantitatively decomposed by chlorine, yielding a diazonium salt and a *substance*, $C_9H_{11}ON_4Cl$. The hydrazone

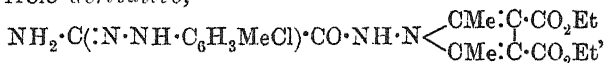
may also be prepared from α -chloroglyoxylamide-3-chloro-*p*-tolylhydrazone.

α -Aminoglyoxylhydrazide-3-chloro-*p*-tolylhydrazone,



colourless prisms, m. p. 199° , prepared by the action of hydrazine hydrate on the corresponding ester, is immediately decomposed by nitric acid, and undergoes oxidative fission by chlorine in a complicated manner, yielding large amounts of diazo-compound. The hydrazide readily yields compounds with benzaldehyde (yellow, rhombic leaflets, m. p. 203°), *p*-hydroxybenzaldehyde (pale yellow needles, m. p. 245°), *m*-hydroxybenzaldehyde (crystalline powder, m. p. 234°), 2:5-dichlorobenzaldehyde (yellow prisms, m. p. 262°), vanillin (small, colourless needles, m. p. 215°), and, less readily, with acetophenone (long needles, m. p. 229°). In each case, fission by chlorine occurs in two stages: (1) evolution of nitrogen, and (2) formation of diazonium salt. The compound with acetophenone is further remarkable for the ease with which it is decomposed into its constituents by concentrated hydrochloric acid.

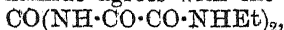
The hydrazide reacts also with ethyl diacetylsuccinate to yield the pyrrole derivative,



almost colourless rhombohedra, m. p. 228° . The compound is decomposed by nitric acid, yielding a diazonium salt, and also by chlorine; in the latter case, nitrogen is not evolved, the products being a diazonium salt and a residue containing the pyrrole nucleus.

H. W.

Diketopiperazines. VII. Action of Oxalyl Chloride on Alkylloxamides. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 215—217. Compare A., 1916, i, 635, 636, 672; 1918, i, 188, 189).—When alkylloxamides are heated with oxalyl chloride under reflux, they yield tetraketo-1-alkylpiperazines. Thus, methylloxamide forms the known methyl derivative, $\text{NMe} \begin{matrix} \text{CO}\cdot\text{CO} \\ \text{CO}\cdot\text{CO} \end{matrix} \text{NH}$, which confirms the constitution of this compound (*ibid.*, 636), whilst tetraketo-1-ethylpiperazine crystallises in small leaflets, m. p. 235° . Using benzene as a diluent, however, the compound obtained from ethylloxamide agrees with the formula

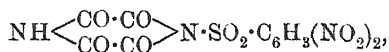


and has m. p. 175° (clear at 187°). Oxamide itself does not undergo such reactions.

J. C. W.

Diketopiperazines. VIII. Action of Absolute Nitric Acid on 3:5-Diketo-1-benzenesulphonylpiperazine. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 218—220).—3:5-Diketo-1-benzenesulphonylpiperazine is very stable towards

pure nitric acid, with which it only reacts on boiling, the product being a *compound*, probably of the formula

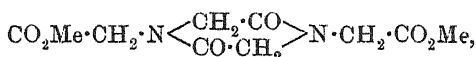


which forms a frothy mass at 124°, becoming clear at 130°.

The piperazine derivative was obtained by Johnson's method (A., 1906, i, 157) after the following alternative process was found to be fruitless. Methyl iminodiacetate is converted into its *benzenesulphonyl* derivative, needles, m. p. 55—57°, and then into *benzenesulphoniminodiacetamide*, $\text{SO}_2\text{Ph} \cdot \text{N}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, needles, m. p. 164°, which only loses a little ammonia when kept molten for an hour, and yields scarcely any sublimate when heated at 350°/10 mm.

J. C. W.

Diketopiperazines. IX. Action of Absolute Nitric Acid on 3:5-Diketo-1-ethylpiperazine. J. V. DUBSKY and F. BLUMER (*Ber.*, 1919, 52, [B], 221—225).—When methyl iminodiacetate is distilled, the residue apparently contains a condensation product, namely, *methyl 2:5-diketopiperazine-1:4-diacetate*,



m. p. 96—97°. The purified distillate (A., 1918, i, 188) is ethylated by means of ethyl sulphate, and the *methyl ethylimino-diacetate*, b. p. 111—113°/8 mm., is converted into *ethylimino-diacetamide*, $\text{NEt}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$, by means of alcoholic ammonia. This has m. p. 137—140°, forms a *hydrochloride*, m. p. 206—208°, and a *nitrate*, m. p. 172°, and when heated at 250°/10 mm. gives a sublimate of 3:5-diketo-1-ethylpiperazine, $\text{NEt} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{array} \text{NH}$, m. p. 74°. This yields a *hydrochloride*, small leaflets, and a *nitrate*, m. p. 145—148°, which dissolves in pure nitric acid to form a *compound*, $\text{C}_4\text{H}_5\text{O}_5\text{N}$, decomp. about 98°. J. C. W.

Diketopiperazines. X. J. V. DUBSKY [with ST. IZDEBSKA-DOMANSKA, M. SPRITZMANN, W. D. VAN LIER-WENSINK, and CH. GRÄNACHER] (*Ber.*, 1919, 52, [B], 225—234).—An account of the preparation of some diketopiperazines and their behaviour towards nitric acid.

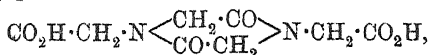
3:5-Diketo-1-phenylpiperazine.—This compound has been made in three ways: (a) by heating equal quantities of aniline and chloroacetamide at 120°, whereby the temperature suddenly rises to 210°, and then sinks again (Bischoff, A., 1889, i, 1015); (b) by heating phenyliminodiacetamide in a vacuum-sublimation apparatus (Bischoff, A., 1898, i, 10); (c) the best way, by heating together chloroacetamide and anilinoacetamide at 100—170°, the latter compound being prepared by heating aniline, chloroacetamide, and fused sodium acetate at 120—140°. When dissolved in ice-cold, absolute nitric acid, the piperazine forms a

yellow *dinitro*-derivative, $C_6H_3(NO_2)_2 \cdot N \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} NH$, decomp. 105° .

3:5-Diketo-1:4-diphenylpiperazine.—Aniline and phenylimino-diacetic acid are condensed to the mono-anilide (Hausdörfer, A., 1889, 1013), and this is heated with benzene and acetic anhydride at 150 — 160° . The 3:5-diketo-1:4-diphenylpiperazine (*ibid.*) yields a mixture of di- and tri-nitro-derivatives with pure nitric acid.

3:5-Diketo-1-p-tolylpiperazine, glistening scales, m. p. 190 — 192° , from *p*-toluidine and chloroacetamide, forms a yellow *dinitro*-compound, m. p. about 110° (decomp.).

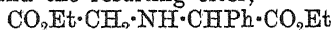
2:5-Diketopiperazine-1:4-diacetic acid,



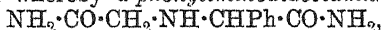
decomp. 280 — 290° , is not affected by solution in pure nitric acid.

2:5-Diketo-1-phenylpiperazine, pearly leaflets, m. p. 245° , obtained by the action of ammonia on chloroacetylphenylglycine (Leuchs and Manasse, A., 1907, i, 770), yields a sulphur-yellow *nitro*-compound, $NO_2 \cdot C_6H_4 \cdot N \begin{smallmatrix} \text{CO} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} NH$, m. p. 247 — 252° .

Some attempts to prepare 3:5-diketo-2-phenylpiperazine are described. In the most successful scheme, glycine ester hydrochloride, benzaldehyde, potassium cyanide, ether, and water were shaken together, and the resulting ester,



(Stadnikoff, A., 1909, i, 106), was left with methyl-alcoholic ammonia at 0° , whereby *α -phenyliminodiacetamide*.



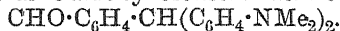
m. p. 152 — 153° , was formed. This did not, however, yield the expected piperazine on sublimation.

J. C. W.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. V. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 541—548).

Condensation Products of *o*-Phthalaldehyde. IV. Condensation of *o*-Phthalaldehyde with Dimethylaniline. ERNST WEITZ (*Annalen*, 1919, 418, 1—28. Compare Thiele and Weitz, A., 1910, i, 854).—This condensation follows very different courses according to the experimental conditions. When *o*-phthalaldehyde, dimethylaniline (more than 6 mols.), and anhydrous zinc chloride are heated together at 120 — 130° for two hours, the chief product is a *substance*, $C_{40}H_{48}N_4$, almost colourless, crystalline powder, m. p. 245° , which can only be the *leuco*-base of *o*-phthalaldehyde-green, $C_8H_4[CH(C_6H_4 \cdot NMe_2)_2]_2$. When *o*-phthalaldehyde, dimethylaniline (2 mols.), and anhydrous zinc chloride are heated together at 100 — 110° for one hour, the chief product is a *substance*, $C_{24}H_{26}ON_2$, crystals, brownish-red when massive, almost

colourless when powdered or in solution, m. p. 143—144°, which is converted into the preceding leuco-base by further heating with dimethylaniline and zinc chloride, reacts additively with acetic anhydride (1 mol.) in the presence of a few drops of sulphuric acid to form the *diacetate*, $C_{28}H_{32}O_4N_2$, m. p. 117—118°, and is therefore regarded as *o*-aldehydoleucomalachite-green,



By oxidation, both *leuco*-bases yield dyes which are almost olive-green.

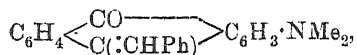
When *o*-phthalaldehyde and dimethylaniline are condensed by heating with concentrated hydrochloric acid on the water-bath, the product is a *substance*, $C_{24}H_{19}O_2N$, garnet-red leaflets, m. p. 163°, which behaves as a weak base (*picrate*, brown crystals, m. p. 170°, decomp. from about 150°). The substance reacts additively with 1 mol. of acetic anhydride (and sulphuric acid), forming a *diacetate*, $C_{28}H_{25}O_5N$, red prisms, m. p. 172°, yields a *nitro*-derivative, $C_{24}H_{18}O_4N_2$, red crystals, m. p. 183°, by treatment with aqueous sodium nitrite in 25% sulphuric acid solution, absorbs 1 mol. of hydrogen in acetone or 70% alcoholic solution by treatment by the Paal-Skita method, and 1 mol. of bromine in glacial acetic acid solution (in neither case could a well-defined additive product be isolated), and yields benzil-2:2'-dicarboxylic acid by oxidation with boiling alkaline permanganate solution. By oxidation in alcoholic solution at the ordinary temperature with 6% hydrogen peroxide solution and 2*N*-sodium hydroxide, the base yields 2-*p*-dimethylaminobenzoylbenzoic acid, *p*-dimethylamino-phenylphthalide, and a *lactone*, $C_{24}H_{19}O_3N$, yellow crystals, m. p. 163°.

On the evidence of the preceding reactions, the red base, $C_{24}H_{19}O_2N$, might be dimethylamino-*o*-aldehydobenzylidene-anthrone, $CHO \cdot C_6H_4 \cdot CH : C < \begin{smallmatrix} C_6H_4 \\ C_6H_3(NMe_2) \end{smallmatrix} > CO$, or 2-*o*-aldehydo-

phenyl-3-*p*-dimethylaminophenylindone, $CHO \cdot C_6H_4 - \begin{smallmatrix} C \cdot CO \\ | \\ NMe_2 \cdot C_6H_4 \cdot C \cdot C_6H_4 \end{smallmatrix}$. Since, however, 10-benzylideneanthrone and 2-dimethylamino-10-benzylideneanthrone (following abstract) respectively yield anthraquinone and 2-dimethylaminoanthraquinone by oxidation, whilst 2:3-diphenylindone yields phenylphthalide and *o*-benzoylbenzoic acid, there can be little doubt that the red base, $C_{24}H_{19}O_2N$, is 2-*o*-aldehydophenyl-3-*p*-dimethylaminophenylindone. C. S.

Some Anthrone Derivatives. E. WEITZ (*Annalen*, 1919, 418, 29—35).—2-Dimethylaminoanthrone is best obtained by heating 2-*p*-dimethylaminobenzoylbenzoic acid with 96% sulphuric acid for one hour at 65—70° (the higher limit must not be exceeded), pouring the cooled solution into water, and neutralising with sodium carbonate. When heated with benzaldehyde (1 mol.) in pyridine containing a few drops of piperidine in a sealed tube at 100°, or, less satisfactorily, with concentrated hydrochloric acid on the water-

bath, it yields 2-dimethylamino-10-benzylideneanthrone,



red needles, m. p. 173°. The latter in alcoholic solution is oxidised to 2-dimethylaminoanthraquinone by 5% hydrogen peroxide and 2*N*-sodium hydroxide. Benzylideneanthrone under similar conditions of oxidation yields anthraquinone and a substance, $\text{C}_{21}\text{H}_{14}\text{O}_2$, colourless crystals, m. p. 133°, which is possibly benzylidene-

anthrone oxide, $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}(\text{CHPh}) \end{array} \text{C} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{CO}.$

C. S.

3-Methyluric Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, 52, [B], 768—784).—It has been recently shown (Biltz and Heyn, A., 1917, i, 291) that δ -, α -, and ζ -methyluric acids are in reality 3-methyluric acid, a mixture of 3-methyluric acid with about 25% 9-methyluric acid and a mixture of 90% of the 3- with 10% of the 9-isomeride respectively. The present communication contains further data in this connexion.

Traube's acid is shown to be 3-methyluric acid, and his process affords the best means of preparing this substance.

The action of chlorine on 3-methyluric acid has been further studied with larger quantities of material; when moisture is carefully excluded, a crystalline 5(4)-chloro-3-methylisouric acid is obtained, which slowly decomposes above 150° and which is reduced by potassium iodide to 3-methyluric acid. Like the amorphous preparation previously described, it is converted by methyl and ethyl alcohols into the corresponding glycol ethers, m. p.'s 207° (decomp.) and 203° (decomp.) respectively. Attempts to convert it into 5(4)-alkyloxy-3-methylisouric acids or 3-methyluric glycol diethers were unsuccessful. It is converted by water into methylalloxan and carbamide, a reaction which is of interest, since it affords an explanation of the ready isolation of 5-chloro-9-methyl- ψ -uric acid from crude α -methyluric acid, the 3-methyluric acid in these circumstances being transformed into products which are readily soluble. In complete absence of moisture, chlorination of the " α "-acid proceeds differently, the 3-methyluric acid being converted into chloro-3-methylisouric acid, whilst 9-methyluric acid yields a product closely allied to the parent substance, probably either 4-chloro-9-methyl- $\Delta^{5:7}$ -isouric acid or 9-methyluric acid 4:5-dichloride.

Attempts are described to isolate 3-methyl- and 9-methyluric acids from " α -methyluric acid" by means of the chloropurines. The action of phosphoryl chloride appears to follow a similar course with each isomeride, and separation was not found possible by conversion into chloropurines and regeneration of the acids from these by means of hydrochloric acid. The chloropurines, however, could be separated by means of their barium salts. From the more sparingly soluble, 8-chloro-3-methylxanthine, decomposing at 344°, was obtained, whilst the more soluble salt yielded 2:6-dichloro-8-

hydroxy-9-methylpurine, decomposing at 275—276°. The latter is quantitatively converted by hydrochloric acid into 9-methyluric acid, but the corresponding yield of 3-methyluric acid is poor. The process affords further evidence of the nature of " α -methyluric" acid, but is without quantitative or preparative significance.

The solubility of derivatives of uric acid in boiling water is frequently described as a means of identification or differentiation. For this purpose, highly accurate values are not required provided that all determinations are performed in a uniform manner. The authors recommend the gradual addition of weighed amounts of finely powdered material to a known volume of water, which is kept gently boiling; the saturation point is regarded as attained when a permanent uniform turbidity appears through the whole solution.

H. W.

α -, ζ -, and δ -Methyluric Acids. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, **52**, [B], 784—804).—The three "isomeric" 3-methyluric acids have been recently examined by Biilmann and Bjerrum (*A.*, 1917, i, 177), who have been led to conclusions differing somewhat considerably from those of Biltz and Heyn (*A.*, 1917, i, 291); the authors have therefore re-examined these acids and repeated much of the work of the Danish chemists. The chief results may be summarised as follows.

ζ -Methyluric acid differs from 3-methyluric acid. It is not a definite chemical compound, but consists rather of mixed crystals of 3-methyluric acid monohydrate and (about 5%) 9-methyluric acid monohydrate. In its properties it closely resembles 3-methyluric acid, but is slightly more soluble in water and rather more easily attacked by phosphoryl chloride.

α -Methyluric acid is also a mixture of 3- and 9-methyluric acids containing about 30—35% of the latter (that is, rather more than had been previously found). In no case is an equimolar compound formed. A crystallisation compound, possibly formed from two molecules of the 3-methyl acid and one molecule of the 9-methyl acid, together with two molecules of water of crystallisation, appears to be formed in small amount. This view is supported by the observation that α -methyluric acid, when crystallised by the method of Biilmann and Bjerrum or by the authors' process, separates in large, shining platelets, which, when further crystallised, appear to be perfectly uniform. On the other hand, however, the relative proportion of the two isomerides seems to vary somewhat, and the water content is scarcely sufficiently constant for a definite chemical compound; in addition, the results of thermo-analytical investigation, which must be received with caution, are opposed to the idea of a compound. It is not at present possible to decide definitely between the two possibilities, mixed crystals or compound, but the authors incline to the former.

The increase in solubility due to admixture, and observed in some instances with α -methyluric acid, as compared with 3- and 9-methyluric acids, is interesting. Similar cases appear to have

been seldom investigated. The increased solubility of salicylic acid in the presence of dextrose, ethyl alcohol, and isobutyl alcohol has, however, been examined by Hoffmann and Langbeck (A., 1905, ii, 374), whilst Störmer, Grimm, and Laage (A., 1917, i, 647) have observed that stereoisomeric β -alkylcinnamic acids yield difficultly separable mixtures of lower solubility. * H. W.

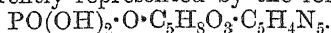
Substances which Inhibit the Coagulation of Proteins by Heat. G. MUNARETTO (*Arch. Pharm. experim.*, 1912, 460—468, 469—479; from *Bied. Zentr.*, 1919, 48, 128).—Formaldehyde and sulphurous acid are the most active inhibiting agents. Other reducing agents, arsenious acid, hydrogen sulphide, and sodium nitrite, are inactive. The addition of sulphurous acid or formaldehyde raises the viscosity of protein solutions. Ox serum becomes gelatinous on contact with sulphurous acid at the ordinary temperature. These effects suggest that a process of denaturation occurs. J. C. D.

Action of Acid and Alkali on Gluten. L. J. HENDERSON, EDWIN J. COHN, P. H. CATHCART, J. D. WACHMAN, and W. O. FENN (*J. Gen. Physiol.*, 1919, 1, 459—472).—Measurements of the hydrogen-ion concentration of solutions which had been in contact with powdered gluten show that the hydrogen-ion concentration in such systems is determined by the ratio of gluten to acid or base. The conclusion is reached that in systems containing gluten and acids or bases, the formation of salts, in accordance with the requirements of the mass law, is the fundamental phenomenon. Measurements were also made of the swelling and viscosity of the gluten component of such systems. The results indicate that simple chemical phenomena are most important in these systems, and that modifications of these, resulting from colloidal and heterogeneous characteristics, are of secondary importance in determining the condition of equilibrium, although somewhat more significant in the progress of the system toward the condition of equilibrium. J. C. D.

Steric Hindrance of Methyl Groups in the Nucleus. WOLFGANG HEUBNER (*Biochem. Zeitsch.*, 1919, 93, 395—396).—Certain aniline derivatives induce blood changes, with the formation of methæmoglobin, when administered to animals. This toxic action may be greatly reduced by the introduction of two methyl groups in the ortho-ortho- or the ortho-para-positions to the nitrogen group (compare A., 1913, i, 786). It is considered that the steric hindrance of the methyl groups prevents oxidation of the nitrogen group, which the author holds is necessary before methæmoglobin can be formed. J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*J. Pharmacol. Exp. Ther.*, 1918, 12, 253).—A crystalline

product, $C_{10}H_{14}O_7N_5P.H_2O$, has been prepared from yeast-nucleic acid. It is soluble in hot water, but very slightly so in cold. It gives the colour reactions for pentose and forms a brucine salt with two equivalents of brucine. Hydrolysis with dilute sulphuric acid yields adenine, but no guanine. Its entire phosphoric acid is readily split, so that it contains neither a cytosine nor a uracil group. It is apparently represented by the formula



J. C. D.

Amphoteric Colloids. II. Volumetric Analysis of Ion-Protein Compounds; the Significance of the Isoelectric Point for the Purification of Amphoteric Colloids. JACQUES LOEB (*J. Gen. Physiol.*, 1918, 1, 237—254).—At the isoelectric point, $p_H = 4.7$, gelatin is practically not dissociated at all. By volumetric analysis, it has been shown that on the alkaline side of the isoelectric point gelatin can combine with cations only, whilst on the acid side it can combine with anions only. At the isoelectric point, gelatin (and probably amphoteric colloids generally) must give off any ion with which they are combined. The simplest method for obtaining these colloids approximately free from inorganic impurities would therefore seem to consist in bringing their hydrogen-ion concentration to that characteristic of their isoelectric point. When gelatin is in combination with univalent ions (Ag, Br, CNS), the curve representing the amount of ion-gelatin present is approximately parallel to the curves for swelling, osmotic pressure, and viscosity. This proves that the influence of the ions on these properties is determined by the chemical or stoicheiometrical, and not by the "colloidal," properties. The sharp drop of these curves at the isoelectric point finds its explanation in the equal drop of the water-solubility of pure gelatin. It is not yet possible to state whether this is merely due to a lack of ionisation of gelatin or to the formation of a tautomeric or polymeric compound. A slight change in the hydrogen-ion concentration increases the water-solubility of gelatin near the isoelectric point. This is not produced by treatment with any other kind of univalent or multivalent ion, and it is considered that this is in harmony with a chemical conception of proteins rather than with the adsorption theory of colloids.

J. C. D.

Amphoteric Colloids. III. Chemical Basis of the Influence of Acid on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 363—385. Compare preceding abstract).—The influence of hydrobromic acid on the physical properties of gelatin has a purely chemical or stoicheiometrical basis. Gelatin is an amphoteric colloid which is sparingly soluble in water at its isoelectric point, whilst transformation into a salt with a univalent ion makes it soluble. Hence the curves representing the changes in osmotic pressure, viscosity, and swell-

ing of gelatin are approximately parallel to those representing the amount of bromine bound by the gelatin.

Titration with sodium hydroxide of gelatin, previously treated with hydrobromic acid, and therefore being on the acid side of its isoelectric point, results in the neutralisation of the pure gelatin (NaOH isoelectric) with sodium hydroxide, and besides in the neutralisation of the hydrobromic acid in combination with the gelatin.

J. C. D.

Amphoteric Colloids. IV. The Influence of the Valency of Cations on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 483—504. Compare preceding abstracts).—The amount of equivalents of metal in combination with 1 gram of a 1% gelatin solution previously treated with an alkali can be ascertained when the excess of alkali is washed away and the hydrogen-ion concentration determined. The results of experiments with lithium, sodium, potassium, ammonium, calcium, and barium hydroxides show that twice as many univalent ions as bivalent cations combine with the same mass of gelatin.

The curves representing the influence of lithium, sodium, potassium, and ammonium on the osmotic pressure (and the other physical properties) of gelatin are identical, using p_H as abscissæ. This contradicts the statements current in colloid chemistry, according to which these four cations have a different effect. The curves for calcium and barium gelatinates are also identical, but differ from those for the univalent metals examined. The ratio of the maximal osmotic pressures of the two groups is 1:3. This means that in a 1% solution of a metal gelatinates there are approximately three times as many particles in solution or suspension when the metal is univalent as when it is bivalent.

The curves representing the conductivities of the same gelatin solutions are almost identical (for the same p_H).

The curves for the viscosity and swelling of barium or calcium and sodium gelatinates are approximately parallel to those for osmotic pressure. The practical identity of the conductivities of metal gelatinates with univalent and bivalent metals excludes the possibility that the differences observed in the osmotic pressure, viscosity, and swelling are determined by differences in degree of ionisation. If it is assumed that compounds of the type $\text{Ca}(\text{gelatin})_2$ exist, the two anions of which can form one aggregate of two gelatin anions, and that such aggregates can form larger aggregates of four, six, and eight gelatin anions, every one of which keeps its original charge, it would be possible to account for the phenomena observed.

J. C. D.

Physiological Chemistry.

Bioelements : The Chemical Elements of Living Matter.

INGO. W. D. HACKH (*J. Gen. Physiol.*, 1919, **1**, 429—433).—The distribution of the elements which enter into the composition of living matter is considered with reference to a new periodic classification (Hackh, A., 1918, ii, 306, 396). J. C. D.

An Indicator Method of Measuring the Consumption of Oxygen.

W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1918, **1**, 167—169).—The blood of *Limulus* when shaken with air absorbs oxygen and turns blue. In the presence of certain organisms which consume oxygen, it is quickly decolorised. A method is described for measuring the time required for the colour change, from which the rate of consumption of oxygen may be determined. J. C. D.

Chemical Studies in Physiology and Pathology. VI. The Biochemistry of Oxidation (Cell Respiration; Oxidising Enzymes; The Theory of Narcosis).

E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **93**, 324—352).—The atoms of the oxygen molecule can be activated by the formation of certain molecular compounds. In aqueous solution, oxygen may form a compound represented by the formula $\begin{matrix} \text{H} \\ | \\ \text{H}-\text{O} \cdots \cdots \text{O} \cdots \cdots \text{O} < \text{H} \\ | \\ \text{H} \end{matrix}$. This linking expresses the activity of the complex H_4O_4 . In this manner, complexes can be formed with water or metals in the form of peroxides. Oxygen bound in this manner can oxidise to carbon dioxide and water many organic substances, such as the lower fatty acids or their salts, without assistance.

The oxidative processes of the body are concerned with the oxidation of simple degradation products derived from the complex proteins, fats, and polysaccharides, and for this purpose the presence of oxygen in the activated form is sufficient. The assumption of the existence of special oxidising enzymes is superfluous. The relationship of these processes to narcosis and respiration is discussed. J. C. D.

The Presence of Calcium in the Red Blood Corpuscles of Ox and Man.

DAVID MURRAY COWIE and HENRIETTA A. CALHOUN (*J. Biol. Chem.*, 1919, **37**, 505—509).—The red blood corpuscles contain calcium, but in a somewhat smaller concentration than the serum (compare Marriott and Howland, A., 1918, ii, 21). J. C. D.

Simultaneous Oxidation of Blood and of Dextrose.

R. FOSSE (*Compt. rend.*, 1919, **168**, 908—910. Compare A., 1912, i, 541).—If, under suitable conditions, the proteins of blood and

dextrose are oxidised simultaneously, there is marked formation of carbamide. The yield of carbamide, formed by the oxidation of blood to which dextrose has been added, increases, within certain limits, with the proportion of dextrose and oxygen consumed. Under suitable conditions, the amount of carbamide formed may reach to 40 grams per litre of blood. W. G.

The Nutritive Value of the Wheat Kernel and its Milling Products. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with the co-operation of EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1919, **37**, 557—601).—The proteins of the entire wheat kernel are not greatly inferior for maintenance to caseinogen, edestin, or even to the total proteins of milk, but they are somewhat superior to gliadin. The wheat proteins considered in their entirety are sufficient for the growth of rats if consumed in sufficient amount. The quantity required is, however, relatively large when comparisons with proteins such as caseinogen are made.

The "crude protein" of commercial wheat embryo meal is more efficient for maintenance than that of the entire kernel or of the endosperm, and it is much more efficient for growth than endosperm protein. The protein of commercial wheat bran may be well utilised (70—75%) by the rat, and if eaten in sufficient amount may be considered somewhat superior to that of commercial embryo and decidedly superior to that of endosperm in promoting growth.

The proteins of the endosperm are adequate for maintenance, but inadequate for growth. Additions of meat, milk, and eggs to wheat flour greatly enhance the value of the proteins of the latter foodstuff for growth.

Commercial wheat embryo is rich in the water-soluble vitamine, but the pure isolated embryos do not appear to contain it. Evidence is given which indicates that the accessory factor is localised in the endosperm, although it is not uniformly distributed throughout it. No confirmation of the existence of a toxic substance in wheat has been obtained (compare Hart, Miller, and McCollum, A., 1916, i, 531).

The question of the degree to which wheat should be milled for general purposes is fully discussed, and the conclusion is reached that, except in special cases, little can be gained by including the bran and embryo in the flour when this is used under the dietary conditions prevailing in the United States. J. C. D.

The Origin of Formic Acid in the Organism. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, **104**, 161—174).—Oxidation of glycerol with potassium permanganate in acid solution may yield as much as 24% of formaldehyde. An increased excretion of formic acid was observed to follow the administration of glycerol. It apparently arises by the intermediate formation of formaldehyde. Glycerophosphoric acid, choline, and lecithin all yield formaldehyde when oxidised by potassium permanganate in acid solution. There is no reason to suppose that the formic acid

excreted in the urine originates from one source. No doubt carbohydrates, glycerol, and lecithin all contribute a certain amount. 3% Hydrogen peroxide will oxidise lecithin, choline, and glycerophosphoric acid, with the formation of formaldehyde.

J. C. D.

Bioluminescence. VII. Reversibility of the Photogenic Reaction in Cypridina. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1918, 1, 133—145).—The author has previously described two photogenic substances from the ostracod crustacean *Cypridina hilgendorfi*, photogenin, which is destroyed by boiling and is non-dialysable, and photophelein, which is stable to boiling and may be dialysed (A., 1917, i, 365). It is now suggested that photophelein is a mixture of two substances, one of which is an oxidisable substance similar to luciferin from *Pholas dactylus* (Dubois, A., 1897, ii, 112). Photogenin is now termed *luciferase*. The term photophelein is retained for a substance present in the extracts which acts by setting free bound or adsorbed luciferin. The action of this substance may be imitated by sodium chloride crystals or saponin. Luciferin is oxidised to *oxyluciferin*, and it is not believed that the change involves a fundamental destruction of the molecule, as it is a reversible process. The change is not analogous to that of hæmoglobin, for it cannot be reversed by reducing the partial pressure of the oxygen. It resembles more closely the oxidation of methylene-blue. The conception of Dubois that luciferin is formed from a precursor proluciferin by the agency of an enzyme coluciferase is held to be incorrect, and the correct explanation is believed to be that oxyluciferin may be reduced to luciferin by a reducing enzyme. Oxyluciferin will pass through a porcelain filter and is dialysable. Luciferin does not exhibit reducing properties similar to those of dextrose.

J. C. D.

Bioluminescence. IX. Chemical Nature of Cypridina Luciferin and Cypridina Luciferase. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, 1, 269—293).—Of a large number of enzymes investigated, only those possessing a proteolytic activity had any digestive effect on luciferase, whilst none had any action on luciferin. A study was made of the "salting out" of luciferin and luciferase, as well as of their solubilities in various solvents, and their behaviour when treated with certain precipitants. Both substances are somewhat readily adsorbed by bone-black, kaolin, and colloidal ferric hydroxide. Consideration of the results obtained in this investigation leads to the opinion that luciferin is a protein on the border-line between the proteoses and peptones, whilst luciferase is regarded as being a more complicated protein, but not a globulin.

J. C. D.

Pharmacology of the Ureter. VI. Action of some Optical Isomerides. DAVID I. MACHT (*J. Pharmacol. and Exp. Ther.*, 1918, 12, 255—263).—*l*-Hyoscamine and *l*-hyoscyne stimulate

the contractions of the ureter, whereas *d*-hyoscamine and *d*-hyoscyne have an inhibitory action. The action of atropine appears to be a summation of the action of the two optically active varieties. Inactive or racemic scopolamine shows an inhibitory action, which is ascribed to the preponderating effect of the *d*-component. *l*-Adrenaline is much more active in stimulating ureteral contractions and raising the tone of the ureters than the racemic variety. *d*-Adrenaline was not examined. *l*-Camphor produced a marked stimulation, but *d*-camphor was apparently inactive. The effect of the racemic form is represented by the arithmetical mean of the two components.

J. C. D.

Isomerism and Anæsthetic Action. J. MORGENROTH (*Ber. Deut. pharm. Ges.*, 1919, **29**, 233—250).—Comparison of the anæsthetic action of eucupine (*isoamylhydrocupreine*) dihydrochloride and *isoamylapohydroquinidine* dihydrochloride shows a quantitative difference between the activity of the stereoisomerides, the former being about twice as potent as the latter. Experiments with eucupine dihydrochloride and eucupinotoxin hydrochloride at different concentrations prove both structural isomerides to have anæsthetic action. The latter does not appear to depend on the intact quinuclidine nucleus, since a pronounced increase in anæsthetising action is coincident with rupture of the carbon-nitrogen bond. The corresponding toxin is far more potent than eucupine, and forms the most powerful anæsthetic known (forty to fifty times stronger than cocaine). It has the power of producing prolonged anæsthesia.

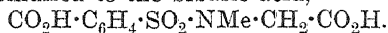
The author is led to the conclusion that the chemotherapeutic action towards trypanosomes, the disinfecting action towards different bacteria, and the anæsthetic action are common to the quinotoxins and to the original alkaloids, and that comparatively all three functions are exerted to a greater degree by the latter. The difference in activity of ethylhydrocupreine and ethylhydrocupreinotoxin towards pneumococci appears to be an exception. Anæsthetic action does not appear to depend actually on space arrangement, since, as shown by the above experiments, the differences are only quantitative. In one instance quoted in the literature, that of benzoyltropeine and benzoyl- ψ -tropeine, a marked difference in anæsthetising action has been attributed to difference in spatial configuration; re-examination of these substances has failed to disclose any difference in their activity.

H. W.

Secondary Action of Arsenic and Salicylic Acid Preparations on the Normal Stomach. BRUNO LEICHTENTRITT (*Zeitsch. physiol. Chem.*, 1919, **104**, 154—160).—According to Klosman (*A.*, 1912, ii, 965), sodium salicylate causes a decreased secretion of gastric juice. This was not confirmed, for it was found that aspirin, sodium salicylate, and salol caused an increased flow. His results with Fowler's solution (liq. potass. arsenic) are, however, confirmed. This preparation, as well as certain organic arsenic

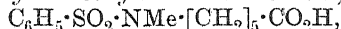
preparations, such as elarson and arsacetin, increased the flow of gastric juice. A similar result was obtained by the administration of preparations containing both iron and arsenic. J. C. D.

A New Instance of β -Oxidation in the Animal Body. KARL THOMAS and HERBERT SCHOTTE (*Zeitsch. physiol. Chem.*, 1919, **104**, 140—153).—Oral administration of *p*-toluenesulphonyl-sarcosine to rabbits results in 80% being excreted in the urine unchanged; 4% is oxidised to the bibasic acid,



81% of benzenesulphonylsarcosine administered in the same manner was recovered from the urine.

ϵ -Benzenesulphonyl- ϵ -methylaminohevoic acid,



prepared from ϵ -methyl-leucine, crystallises from methyl formate and light petroleum in slender, white needles, m. p. 57° . When administered to rabbits, 44% was recovered from the urine as γ -benzenesulphonylmethylaminobutyric acid, oxidation having occurred at the β -carbon atom.

Benzenesulphonylaminobutyric acid, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$, has m. p. 91 — 92° . When methylated with methyl sulphate, it yields *benzenesulphonylmethylaminobutyric acid*, m. p. 84 — 87° . This substance was recovered unchanged from the urine after administration to rabbits. J. C. D.

Detoxication of Inhaled Hydrogen Cyanide by Sodium Thiosulphate. E. TEICHMANN and W. NAGEL (*Biochem. Zeitsch.*, 1919, **93**, 312—323).—The observation of Lang (*Arch. exp. Path. Pharm.*, 1895, **36**, 75) that sodium thiosulphate can protect animals against the toxic effects of hydrogen cyanide is confirmed. The salt is efficient as an antidote when the poison is inhaled by animals. It will be necessary to establish that sodium thiosulphate is not toxic for man before the therapeutic application can be made. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Different Agents on the Saccharifying and Fermenting Powers of *Mucor Boulard*. BETTINGER and DELAVALLE (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 114—129).—In experiments on the cultivation of *Mucor Boulard* on sugared extract of malt combs, the development of acid was found to be in direct proportion within limits to the access of air and the sugar content. Comparatively low temperatures gave the highest results. Succinic acid is the only non-volatile acid formed, whilst acetic acid mainly constitutes the volatile acidity. Nitrogenous matter

at first retards, but later accelerates, saccharification, peptone and asparagine giving the best results, whereas ammonium sulphate has a comparatively slight effect in this direction. Calcium and potassium phosphates, and to a less degree ammonium phosphate, accelerate saccharification, but sodium phosphate produces little or no result.

J. P. O.

The Sensitiveness of Living Yeast to H^+ and OH^- Concentration. H. VON EULER and F. EMBERG (*Zeitsch. Biol.*, 1919, 69, 349—364).—Fermentation by the living cell is not effected solely by zymase, but is bound up to a large extent with the life of the cell itself. From the investigation of a bottom yeast, it is shown that the sensitiveness to acid and alkali of the process of inversion by the living yeast cell is not appreciably different from the sensitiveness of the isolated enzyme. It is therefore possible to conclude that the enzyme exists in the free state in the cell. The influence of growing the bottom yeast at different hydrogen-ion concentrations (p_H 3.5—3.8 and 6.6—7.2) on the characteristic cellular activities has been studied. The inverting action was little affected, but appreciable changes in the rate of growth and composition of the cells were noted.

J. C. D.

Changed Course of Alcoholic Fermentation in an Alkaline Medium. ALICE OELSNER and ALFRED KOCH (*Zeitsch. physiol. Chem.*, 1919, 104, 175—181).—The authors have failed to confirm the statements of Wilenko (A., 1917, i, 680) that the course of the fermentation of sugar in an alkaline phosphate medium is changed and that no carbon dioxide is formed under those conditions. The alkalinity delays the fermentation, but alcohol and carbon dioxide are always obtained. The observation of Neuberg and Färber (A., 1917, i, 502) that more aldehyde is produced when the fermentation is conducted in an alkaline medium is confirmed.

J. C. D.

The Temperature-coefficient of Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*J. Gen. Physiol.*, 1919, 1, 295—298).—The temperature-coefficient of photosynthesis in *Ulva rigida* between 17° and 27° is 1.81. It is suggested that photosynthesis involves catenary reactions of the type $S \rightarrow M \rightarrow P$, in which S represents a substance which, under the influence of light, breaks down to form M ; this in turn forms P , the amount of which is proportional to the amount of photosynthesis. If the reaction $S \rightarrow M$ is more rapid than $M \rightarrow P$, the speed of the reaction as a whole will depend chiefly on the speed of the change $M \rightarrow P$.

The effect on the whole reaction of a rise of temperature will therefore depend chiefly on its effect on the second reaction. It is therefore not surprising to find a high temperature-coefficient for photosynthesis. Analogous cases exist in photochemistry.

J. C. D.

Permeability in Plants. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 299—304).—Certain conclusions concerning the behaviour of protoplasm drawn from the results of experiments on *Laminaria Agardhii* (compare A., 1918, i, 470) have been confirmed by experiments with a red alga (*Rhodymenia palmata*), a green alga (*Ulva rigida*), and a flowering plant (*Zostera marina*).
J. C. D.

Decrease of Permeability and Antagonistic Effects caused by Bile Salts. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 405—408).—The results of experiments on the electrical conductivity of *Laminaria* indicate that sodium taurocholate is able to produce a decrease in permeability and to antagonise sodium chloride. This confirms the hypothesis that antagonistic relations can be predicted from studies on the permeability of pure substances.
J. C. D.

A Comparison of Permeability in Plant and Animal Cells. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 409—413).—The author has made quantitative studies of the permeability of plant cells as represented by *Laminaria*, and animal cells as represented by the skin of frogs (*Rana pipiens*). Both tissues showed a closely similar behaviour, and this agreement indicates that the conclusions drawn from a study of *Laminaria* are of general application. It would appear that the physiological characteristics brought to light by these studies belong to the fundamental properties of protoplasm.
J. C. D.

Effect of certain Compounds of Barium and Strontium on the Growth of Plants. J. S. MCHARGUE (*J. Agric. Res.*, 1919, 16, 183—194).—Barium or strontium carbonate in the absence of calcium carbonate is toxic to plants, the former having a greater toxicity than the latter, but in the presence of calcium carbonate they appear to exert a distinct stimulating influence on the growth of the plants studied. Barium sulphate is much more toxic than barium carbonate. Neither barium nor strontium can replace calcium as a plant food. The root growth is accelerated in all cases where barium or strontium carbonate is added to the sand in which the plants are growing.
W. G.

The Identification, Localisation, and Distribution of Oxalic Acid [Soluble Oxalates] in Plants. NORBERT PATSCHOVSKY (*Ber. Deut. bot. Ges.*, 1918, 36, 542—548).—The usual method of detecting the presence of soluble oxalates in cell sap by means of potassium salts suffers under the disadvantages that the potassium oxalate crystals are not very characteristic, and that they are liable to be completely obscured by co-precipitated tannins. The author finds ferrous sulphate or ferrous ammonium sulphate to be a more suitable reagent; the not too thin section is immersed on an object-glass in an acetic acid solution of the ferrous salt (10%), covered

with a slip, and gently warmed to expel air; in the presence of oxalates, ferrous oxalate separates after a time in crystals, the size of which is about $15 \times 9 \mu$. Larger crystals may be obtained by delaying the separation by addition of sodium acetate, sucrose, or gelatin.

The localisation of oxalates is best effected by injecting a highly concentrated ferrous solution into the plant by means of an air pump; under these conditions, precipitation of ferrous oxalate occurs within the cell, whilst with less concentrated solutions the oxalates diffuse through the cell wall, and precipitation takes place in the intercellular region.

The ferrous reagent has the further advantage of allowing a simultaneous detection of tannins.

The author has applied the method to a large number of plants; for details, the original paper must be consulted. H. W.

Action of Coal Gas on Plants. V. Action on Trees. Hydrocyanic Acid as the most Detrimental Constituent of Gas. C. WEHMER (*Ber. deut. Bot. Ges.*, 1918, 36, 460—464. Compare A., 1917, i, 618; this vol., i, 114).—Continuing his previous experiments on the action of coal gas on the root systems of trees, the author now finds that in many instances in which the detrimental action is not immediately apparent, the effects are observed at the end of the period of winter rest, when in almost every instance the tree is killed. The most detrimental constituent of coal gas is now proved to be hydrogen cyanide; the toxicity of gas-water is shown to be exactly similar to that of a hydrocyanic acid solution of equivalent concentration, and, further, the violent toxic action of coal gas is not observed if the gas is passed through a solution of alkali hydroxide and ferrous sulphate. Cress is extraordinarily sensitive to minute traces of hydrocyanic acid. H. W.

A Purely Mineral Solution Capable of Assuring the complete Evolution of Maize Cultivated and Sheltered from Bacteria. P. MAZÉ (*Ann. Inst. Pasteur*, 1919, 33, 139—173).—From a series of water-culture experiments, the author finds that, in addition to nitrogen, phosphorus, potassium, calcium, magnesium, sulphur, iron, chlorine, silicon, manganese, and zinc, boron, aluminium, fluorine, and iodine are equally essential to the development of maize. Organic substances, excluding the organic reserves of the seed, although not indispensable, exert a beneficial influence on the growth of the plant when added to the mineral nutrient solution. It is advisable that the iron should be present in the ferric state in the culture solution, or that some oxidising agent should be present. Insufficient aeration of the culture solution exerts an unfavourable influence on the vegetation. W. G.

Organic Chemistry.

Electrolytic Preparation of Chloroform. JOSEF FEYER (*Zeitsch. Elektrochem.*, 1919, **25**, 115—145).—The electrolytic preparation of chloroform from alcohol and from acetone has been investigated under various conditions, particularly in solutions of alkali chlorides and chlorides of the alkaline earth metals. It is shown that the methods put forward in the literature for the electrolytic preparation of chloroform from acetone are inaccurate in their details on account of imperfect methods of analysis. It is also shown that the present methods of isolating the chloroform are imperfect; this applies both to the method of absorption of the chloroform in alcohol and to the distillation method. Both methods involve considerable loss of material. Pure chloroform can only be directly obtained by freezing it out of its mixture with hydrogen by means of solid carbon dioxide and ether. The present methods of electrolysis are inefficient, because the alkali produced in the process decomposes considerable quantities of chloroform. By using a neutralisation cathode, it is possible to prepare chloroform from acetone in yields amounting to 65% of the current. When platinum electrodes are used, a material yield of 75—80% is obtained with a current density of 1.1 amp./sq. cm. at the anode and 0.5 amp./sq. cm. at the cathode. The primary reaction in the electrolysis is the formation of hypochlorite, which is followed by the reaction $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 + 3\text{HOCl} = \text{CHCl}_3 + \text{CH}_3\cdot\text{CO}_2\text{H} + 2\text{H}_2\text{O}$. Methyl ethyl ketone and higher ketones react in the same way with electrolytic hypochlorite. The method for the preparation of chloroform from alcohol put forward by Trechzinsky (A., 1907, i, 270) is criticised and shown to be inaccurate. In the case of alcohol, it is also possible by the introduction of a neutralisation cathode to obtain considerable yields of chloroform at temperatures between 25° and 35° when a current density of 1 amp./sq. cm. is used on the anode and 1.5 amp./sq. cm. on the cathode. A current yield of 77% and a material yield of 82% were obtained under these conditions. The maximum yield is obtained at temperatures between 25° and 30°. The preparation of chloroform from acetone or alcohol in calcium chloride solution only proceeds well when specially prepared nickel or copper cathodes are used. These electrodes are prepared by immersing ordinary nickel or copper electrodes in concentrated nitric acid for a few moments and then washing with water. Using these electrodes, a current yield of 71% and a material yield of 80% were obtained from acetone in calcium chloride, whilst with alcohol in calcium chloride the material yield was 99% and the current yield 90%. The formation of chloroform from alcohol occurs in three stages: first, an oxidation of the alcohol to aldehyde; secondly, a formation of hypochlorite; and thirdly, an interaction between the

aldehyde* and the hypochlorite: (i) $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} + \text{HOCl} = \text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O} + \text{HCl}$; (ii) $\text{OH}' + \text{Cl}_2 = \text{H}' + \text{Cl}' + \text{ClO}'$; (iii) $\text{CH}_3\cdot\text{CHO} + 3\text{HOCl} = \text{CHCl}_3 + \text{HCO}_2\text{H} + 2\text{H}_2\text{O}$; (iv) $\text{H}\cdot\text{CO}_2\text{H} + \text{HOCl} = \text{CO}_2 + \text{H}_2\text{O} + \text{HCl}$. It is shown that equation (i) is partly replaced by the reaction $\text{CH}_3\cdot\text{CH}_2\cdot\text{OH} + \text{O} = \text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O}$.

J. F. S.

Substitution by Halogens in the Aliphatic Series. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, 10 pp.; from *Chem. Zentr.*, 1919, i, 221).—The catalytic influence of light on the process of chlorination probably depends on the formation of the complex, Cl_3 , in illuminated chlorine. The catalysing action of water is attributed to the production of a hydrate, $\text{H}_2\text{OCl}_2 + n\text{H}_2\text{O}$, which only actually separates below 0° , but is assumed to be capable of transitory existence at a higher temperature. The presence of water during chlorination is particularly advantageous in the treatment of readily volatile hydrocarbons. The method of moist chlorination has been applied in particular to substituted hydrocarbons, such as ethyl chloride, *iso*amyl chloride, ethylene chloride, chloroform, propyl bromide, ethylene bromide, ethyl iodide, toluene, and xylene.

H. W.

Organic Chemical Reagents. IV. The Preparation of Alkyl Iodides. ROGER ADAMS and V. VOORHEES (*J. Amer. Chem. Soc.*, 1919, 41, 789—798).—The usual laboratory methods for the preparation of the alkyl iodides are unsuitable when dealing with large quantities of material. The rapid preparation of methyl, ethyl, *n*-butyl and *iso*amyl iodides (in quantities of 3—4 kilos.) according to a modification of Walker's method (T., 1892, 61, 717) is fully described, along with a detailed account of the apparatus employed. *n*-Propyl iodide was prepared in smaller amount.

The suitable alcohol is heated in a large, round-bottomed flask of about 12 litres capacity with a mixture of approximately equal amounts of red and yellow phosphorus. The vapours evolved are condensed in contact with iodine, and are then returned to the flask. The use of a certain amount of yellow phosphorus is particularly advantageous, the reaction then being instantaneous and the colour of the iodine disappearing immediately on reaching the reaction flask. During the subsequent distillation of the alkyl iodides, the troublesome frothing which occurs when only red phosphorus is employed is absent. Further quantities of iodine can be introduced without dismantling the apparatus, and it is possible to prepare more than 6 kilos. of crude iodide in a day, using enough phosphorus and alcohol for four portions of iodine of $1\frac{1}{2}$ kilos. each. Five such apparatus can easily be run simultaneously, producing 30 kilos. of crude product in a day.

In the case of butyl and amyl alcohols, the reaction proceeds extremely readily, owing to the great solvent action of these compounds on iodine at their boiling point. A small amount of yellow

phosphorus is always left behind, but phosphonium compounds do not appear to be formed. The yields are in every case 90—100% of the theoretical.

In the preparation of the lower alkyl haloids, a large excess of alcohol may be used, but in the case of the higher alcohols this must be avoided, as otherwise difficulties arise in the purification of the product.

F. C.

Nitroethylene. HEINRICH WIELAND and EUKLID SAKELLARIOS (*Ber.*, 1919, 52, [B], 898—904).—*Nitroethylene* can be prepared in 50% yield by the dehydration of β -nitroethyl alcohol by phosphoric oxide or sodium hydrogen sulphate; it is an almost colourless, mobile liquid, b. p. 98.5° , $D_{13.8}^{20}$ 1.073, the vapour of which violently attacks the eyes and throat. It readily undergoes polymerisation; this occurs slowly when the pure substance is preserved, more rapidly on exposure to light. The process is remarkably catalysed by water, so that a freshly prepared aqueous solution of the substance becomes cloudy almost immediately, and the separation of the polymeride is complete in a few minutes (the substance cannot be depolymerised to nitroethylene by heat); polymerisation is retarded by acid, but in these circumstances a slow reaction with water occurs, with formation of β -nitroethyl alcohol. With alkali, polymerisation occurs with explosive violence. Reduction with stannous chloride and hydrochloric acid yields acetaldehyde and hydroxylamine, whilst with zinc dust and acetic acid ethylamine is produced. Nitroethylene unites immediately with bromine in ethereal solution, yielding *nitroethylene dibromide*, colourless liquid, b. p. $97^\circ/21$ mm., and with aniline giving *N- β -nitroethylaniline*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NO}_2$, colourless leaflets, m. p. 37° (the *hydrochloride* is described).

[With E. BLÜMICH.]—Attempts to prepare nitroethylene by the elimination of hydrogen bromide from bromonitroethane by methylalcoholic potassium hydroxide were unsuccessful, the products being potassium bromide, potassium nitrite, and the *potassium* salt of dinitroethane, shining, golden needles which explode at about 150° ; *aa-dinitroethane* has b. p. $72^\circ/12$ mm.

H. W.

The Specific Gravity and Refractive Power of Solutions of Glycerol. H. WOLFF (*Zeitsch. angew. Chem.*, 1919, 32, 1, 148).—The author has determined the density and refractive indices of solutions in water of an extremely pure sample of glycerol, with the following results:

86% *Solution*.— D_{15}^{20} 1.2294, n_D^{20} 1.4545, n_D^{15} 1.4537, $n_D^{17.5}$ 1.4533; change in refractive index per $^\circ\text{C}$., 2.8×10^{-4} .

76.77% *Solution*.— D_{15}^{20} 1.2043, D_{15}^{20} 1.2036, D_{15}^{20} 1.1998, the coefficient of expansion being 0.000463. n_D^{20} 1.4401, n_D^{15} 1.43945, $n_D^{17.5}$ 1.4388; change in refractive index per $^\circ\text{C}$ = 2.6×10^{-4} .

The results agree very closely with those contained in Gerlach's table, but not so closely with those of Lenz, Strohmer, and Skalweit, although there is fair agreement with the latter.

J. S. G. T.

New Initial Materials for the Preparation of Allyl Compounds. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, 3 pp., from *Chem. Zentr.*, 1919, i, 221).—A mixture of glycerol and formic acid (95%) is heated for four hours under reflux in the presence of a small quantity of ammonium chloride as catalyst, and the product is fractionally distilled. At above 190°, the glycerol diformin primarily formed breaks down into allyl formate, water, and carbon dioxide, and decomposition is complete at 260°. Allyl chloride is obtained in good yield when cold allyl formate containing 10% of dissolved zinc chloride is treated with hydrogen chloride and the mixture is subsequently heated on the water-bath. H. W.

Action of Heat on the Alkali and Alkali-Earth Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 168, 1054—1056).—Potassium methyl sulphate when heated at 220°, rising slowly to 280°, is decomposed almost quantitatively into potassium pyrosulphate and methyl ether. At a slightly lower temperature sodium methyl sulphate behaves similarly, but at the higher temperature 7% of the salt is decomposed into sodium sulphate and methyl sulphate. This second reaction with the formation of the two sulphates is the principal one, and occurs below 200° in the case of calcium, barium, and lithium methyl sulphates, and slowly in the cold in a desiccator in the case of strontium methyl sulphate. W. G.

Alcoholysis. AD. GRÜN, FRANZ WITTKA, and EMIL KUNZE (*Chem. Umschau Fett-Ind.*, 1917, 24, 15—16, 31—34; from *Chem. Zentr.*, 1919, i, 222—223).—The authors have investigated the direct conversion of fats into the ethyl esters of their fatty acids by boiling them with alcohol containing a small amount of mineral acid. Alcoholysis in an acid medium is found to be a consecutive process, thus showing that the hydrolysis of fats proceeds by separate steps in every case. Pure tristearin was obtained by the catalytic reduction of almond or sesame oil and removal of oleodistearin and free fatty acid by washing with light petroleum and boiling with alcohol. The best results were obtained when tristearin (100 parts) was heated for three hours with a 1% solution of sulphuric acid in absolute alcohol (150 parts). The product consisted of a mixture of mono-, di-, and tri-stearin and ethyl stearate, from which the tristearin could readily be removed by crystallisation from alcohol; the separation of the other components was effected after distillation of ethyl stearate under diminished pressure, and was best accomplished by a frequent change of solvent (alcohols in which monostearin is most readily, and light petroleum in which it is least readily, soluble). Three thousand grams of tristearin yielded 400 grams of unchanged material (after repeated alcoholysis of the fraction which had escaped action in the first treatment), 300 grams of distearin, 200 grams of monostearin, more than 1200 grams of ethyl stearate, and 600 grams of mixed frac-

tions. The distearin fraction had m. p. $74\cdot5^{\circ}$, 75° , $75\cdot5^{\circ}$ (it should be noted that a molar mixture of mono- and tri-stearin has the same m. p. as distearin); it was converted by thionyl chloride into distearochlorohydrin, m. p. 56° , described by Grün and Theimer, and appears to be the $\alpha\beta$ -distearin. The monostearin fraction was composed of indistinct crystals, m. p. 79 — 80° , hydroxyl number, 311·4. H. W.

Chemistry of the Glutaconic Acids. XI. The Occurrence of 1:3-Addition to the Normal Form. JOCELYN FIELD THORPE (T., 1919, 115, 679—686).

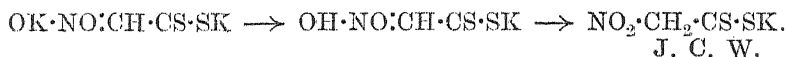
Lactonic Acids. BROR HOLMBERG (*Svensk. Kem. Tidskr.*, 1918, 30, 190—205, 215—222; from *Chem. Zentr.*, 1919, i, 223—224).—In extension of his work on the Walden inversion, the author has investigated the stereochemical and kinetic behaviour of lactonic acids. The hydrolysis of malic acid lactone has been examined from these points of view, and, since the behaviour of β -lactones differs in several respects from that of γ -lactones, the work has also been extended to paraconic acid.

r-Malic acid lactone, shining leaflets or thin plates, m. p. 64 — 65° , is prepared by the action of moist silver oxide on *r*-iodosuccinic acid; *d*-malic acid lactone, colourless syrup, $[\alpha]_D + 41^{\circ}$, in aqueous solution (2·5%), is similarly obtained from *l*-iodosuccinic acid. The rate of hydrolysis was measured by dissolving the crude acid in water or dilute nitric acid of the desired concentration and estimating the amount of lactone in the solution by heating a measured portion until hydrolysis was complete and determining the increase in acidity by titration. Autohydrolysis is a rather slow, unimolecular change; nitric acid somewhat increases the velocity of action. In acid solution, *d*-malic acid lactone yields a mixture of *r*- and *l*-malic acids, whilst almost pure *d*-malic acid is formed in alkaline solution.

The formation of paraconic acid by elimination of bromine from salts of itabromopyrotartaric acid is a unimolecular change which is not reversible in dilute solution. As acid salt and to a still greater extent as free acid, itabromopyrotartaric acid is only slowly converted into its lactone. Silver salts catalyse the elimination of bromine in acid solution. The formation of paraconic acid from itamalic acid is reversible. Acid salts of itamalic acid are only slowly converted into paraconic acid, and this is also true of the reverse action in neutral solution. Lactone formation and hydrolysis are catalysed by hydrogen ions. The affinity constants of itamalic acid and paraconic acid are approximately $K=0\cdot0003$ — $0\cdot0004$. The hydrolysis of paraconic acid by alkali is a bimolecular reaction. H. W.

Action of Carbon Disulphide on Nitromethane. ERICH FREUND (*Ber.*, 1919, 52, [B], 542—544).—A mixture of nitromethane and carbon disulphide reacts with alcoholic potassium

hydroxide to give *potassium nitrodithioacetate*, as a brown, crystalline precipitate, decomp. 203.5° . When heated with potassium hydroxide, it yields potassium nitroacetate (Steinkopf, A., 1909, i, 559), and its solutions do not give an acid reaction until one equivalent of acid has been added, this change being interpreted as follows:



Some Metallic Derivatives of Ethyl Thioglycollate.

CHARLES A. ROUILLER (*J. Amer. Chem. Soc.*, 1919, **41**, 777—781).—Ethyl thioglycollate was shown by Rowntree and Abel (*J. Pharmacol.*, 1910, **2**, 108) to dissolve antimonious and mercuric oxides, the hydrogen of the mercaptan group being completely replaced by the metal. The antimony derivative of the ester is an insoluble oil, but the corresponding amide is soluble in water and possesses trypanocidal properties. The author has found that the oxides of bismuth, copper, mercury, silver, zinc, tin, and arsenic react energetically with ethyl thioglycollate. It was hoped to prepare bactericidal substances, which would either be soluble in water or could be used in powder form on wound surfaces. *Triethyl bismuthtrithioglycollate*, $\text{Bi}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_3$, forms small, yellow crystals, m. p. $87-88^{\circ}$, soluble in alcohol. *Diethyl mercuridithioglycollate*, $\text{Hg}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, long needles, m. p. 55° , is identical with the product obtained from mercuric chloride and two molecules of ethyl thioglycollate (Wislicenus, *Annalen*, 1868, **146**, 148). Ethyl silverthioglycollate, yellow needles from acetone, m. p. $75-77^{\circ}$, is with difficulty decomposed by concentrated nitric acid in sealed tubes. The action of silver nitrate on the ester was also investigated. With cupric hydroxide a crystalline substance is obtained which contains less than half the amount of copper to be expected from analogy with the previous reactions. It is very resistant to concentrated nitric acid at $200-270^{\circ}$. F. C.

Constitution of Maltose. A New Example of Degradation in the Sugar Group. JAMES COLQUHOUN IRVINE and JAMES SCOTT DICK (*T.*, 1919, **115**, 593—602).

Inversion of Sucrose by Mechanical Ionisation of Water.

J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1919, **168**, 1125—1128).—If 100 c.c. of a 5% solution of sucrose are passed five times through a Richardson pulveriser, 0.06 gram of invert sugar is obtained. The addition of sodium or potassium chloride appreciably increases the yield of invert sugar. Using a mixture of electrolytes such as is found in the Ringer-Locke solution, a slightly greater increase is obtained, and if a trace of zinc sulphate or, better still, a trace of zinc sulphate and a trace of manganese sulphate is added, the increase is still greater. On the other hand, the presence of a trace of potassium cyanide or of hydrocyanic

acid or of silver nitrate prevents the inversion taking place. The inversion is greater in Raulin's solution than in Locke's solution, and the authors have determined the effect of removing in turn each one of the ingredients of Raulin's solution in the inversion. The results so obtained are in agreement with those obtained by Raulin in his work on *Aspergillus niger*. Similarly, the anti-septics which inhibited the development of *Aspergillus niger* equally checked the inversion of sucrose. The curve showing the relationship between the amount of sucrose inverted and the number of passages through the pulveriser is sinusoidal, but slightly irregular. W. G.

The Composition of Starch. I. Precipitation by Colloidal Iron. II. Precipitation by Iodine and Electrolytes. JOHN MELLANBY (*Biochem. J.*, 1919, 13, 28—36).—When colloidal iron is added to a solution of starch three well-marked phases may be recognised; (i) a portion of the starch is precipitated by the colloidal iron only, (ii) a second portion of the starch is carried down with the colloidal iron when an electrolyte is added, and (iii) the filtrate from (ii) contains unprecipitated starch. Eighty % of the starch is precipitated in the first phase, independently of the amount of iron added. Starch in solution bears a negative charge. From these observations it is concluded that amylogranulose may be divided into three fractions, α , β , and γ , according to their precipitability by colloidal iron.

Quantitative studies of the reaction between starch and iodine indicate that a quantitative reaction takes place between the starch and the ionised iodine. The theory that iodine reacts chemically with starch is strengthened by the fact that the equivalent point is not affected by dilution, temperature, or the precipitating electrolyte. On this basis the least value for n for $(C_6H_{10}O_5)_n$ is 10, assuming that one molecule of starch reacts with one atom of iodine. This value is, of course, only a mean value for a number of starch complexes, such as α , β , and γ granulose, in which n is continually varying. For amylogranulose γ (unprecipitated by colloidal iron), $(C_6H_{10}O_5)_5$ is equivalent to I. After the formation of the starch iodide it may adsorb further quantities of iodine, depending on the iodine concentration of the original mixture. J. C. D.

The Supposed Degradation of Starch by Formaldehyde. MARTIN JACOBY (*Ber.*, 1919, 52, [B], 558—562).—Woker's assumption that formaldehyde resembles diastase in its action on starch is primarily based on the fact that mixtures of starch and formaldehyde soon lose the power of giving a blue colour with iodine (A., 1917, i, 61, 447). It is now shown that the addition of ammonium acetate is quite sufficient to restore this power, whereas it has no influence on the iodine reaction with starch which has been left with diastase (compare also von Kaufmann, *ibid.*, 251).

J. C. W.

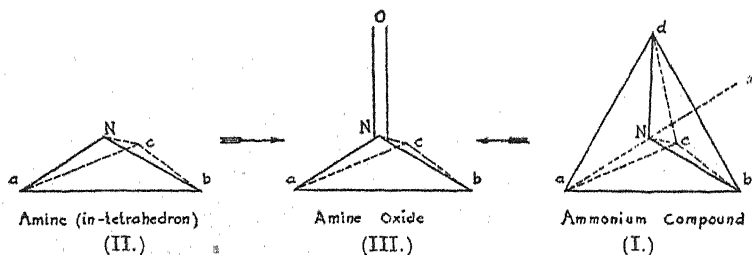
The Nature of Solutions of Starch in Formalin, and the Quantitative Re-conversion of Formalin-Starch into Starch. The Colour of Iodine Solutions. W. VON KAUFMANN and A. LEWITE (*Ber.*, 1919, **52**, [B], 616—627. Compare A., 1917, i, 251).—The fact that solutions of starch and formalin merely contain an additive compound of the two agents and not hydrolytic products as Woker supposed, is proved by the quantitative recovery of absolutely unchanged starch from such mixtures by precipitation with alcohol.

The colorations with iodine which such solutions produce (resembling those given by partly hydrolysed starch) may be explained in the terms of colloid chemistry. If, as Harrison assumes (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 5), the well-known blue colour is the colour of colloidal iodine protected by the starch, then formaldehyde causes a reversible increase in the degree of dispersion, and the addition of electrolytes an aggregation of the particles (the blue colour is restored by electrolytes), which is furthermore hindered by the addition of a protective colloid like gum-arabic.

The colour of iodine solutions in halogen derivatives of methane and ethane changes from brown to violet according as the number of un-substituted hydrogen atoms falls. J. C. W.

Space Representation of Organic Nitrogen Compounds.

PANCHANAN NEOGI (*J. Amer. Chem. Soc.*, 1919, **41**, 622—639).—A theoretical paper, in which it is shown that the properties of nitrogen compounds can only be explained on the assumption of a tetrahedral formula for nitrogen, using the complete figure for quinquivalent nitrogen (I) and the "inner tetrahedron" for trivalent nitrogen (II), thus:



The subjects discussed are as follows. (1) The non-equivalence of the fifth bond, as revealed by the discovery of isomerides of the type $(\text{NMe}_3 \cdot \text{OR})\text{OR}'$ and $(\text{NMe}_3 \cdot \text{OR}')\text{OR}$ (Meisenheimer, A., 1913, i, 595). (2) The non-existence of any isomerides of the types Na_3bax and Na_2bcx , and the existence of only two optical isomerides of the type Nabcdx . (3) The existence of only four optical isomerides in the case of compounds containing one asymmetric carbon

and one asymmetric nitrogen, or two asymmetric nitrogen atoms. (4) The non-existence of isomeric pyridinium and quinolinium compounds and the existence of isomeric tetrahydroquinolinium salts. (5) The failure to resolve amines of the type *Nabc* into optical isomerides has hindered the general acceptance of a space representation for trivalent nitrogen, although the above formula is used to explain the isomerism of the oximes, etc. It also explains why *tert.*-amines of this type give enantiomorphous amine-oxides on oxidation (Meisenheimer, A., 1912, i, 25), these compounds being represented as in (III) above. J. C. W.

Preparation of Diacetoneamine. ARTHUR ERNEST EVEREST (T., 1919, 115, 588—592).

The Mechanism of the Artificial Formation of Carbamide by Oxidation, and the Synthesis of the Natural Principals in Plants. R. FOSSE (*Compt. rend.*, 1919, 168, 1164—1166. Compare this vol., i, 297).—The oxidation of very small amounts of dextrose in strong ammonium hydroxide solution gives rise to considerable proportions of cyanic acid and carbamide. After tautomerisation of the ammonium cyanate by heat the yield of carbamide exceeds 70% of the dextrose used. Much higher yields of carbamide are obtained by oxidising, under the same experimental conditions, formaldehyde or urotropine. The author suggests that in the formation of carbamide from sugars by oxidation, formaldehyde is first formed, and is then converted by the action of ammonia and oxygen into hydrogen cyanide, which is further oxidised to cyanic acid, which with ammonia yields carbamide. W. G.

Certain Metallo - Ferrocyanide Compounds, their Behaviour towards Chlorine and Bromine, and their Use in Analysis. FRANZ FELIX WERNER (*Zeitsch. anal. Chem.*, 1919, 58, 23—24. Compare A., 1912, ii, 687).—*Manganese ferrocyanide.*—A white substance which is coloured green by chlorine water and oxidised to the brown ferricyanide by bromine water. *Nickel ferrocyanide.*—Bluish-green; not attacked by chlorine water, but converted into the brown ferricyanide by bromine water. *Cobalt ferrocyanide.*—An unstable, green compound, which chlorine water oxidises to the ferricyanide; it is decomposed by bromine water, yielding black, hydrated cobalt oxide. *Mercurous ferrocyanide.*—The grey compound is coloured green when treated with chlorine water or bromine water. *Mercuric ferrocyanide.*—White; chlorine water colours it green and bromine water brown. *Bismuth ferrocyanide.*—A yellowish-green compound which is not attacked by chlorine water or bromine water. [See further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

The Benzene Problem. A. VON WEINBERG (*Ber.*, 1919, 52, [B], 928—940).—A theoretical paper, in which the author advances an explanation of the atomic structure of benzene based on the continuous oscillation of the atoms within the molecule. The author considers that in the case of the double bond two valencies of one atom saturate or strive to saturate two valencies of a neighbouring atom in consequence of the oscillation of the atomic nuclei; a considerable amount of evidence in favour of this hypothesis is deduced from consideration of the internal energy, molecular volume, absorption spectra, intramolecular change, and Walden inversion of substances containing unsaturated groups and of the influence of double bonds on the stability of the molecule. The argument is extended to conjugated linkings and thence to benzene; in the latter case the six carbon atoms only lie in one plane as a transitory phase; otherwise, the atoms 1, 3, 5 and the atoms 2, 4, and 6 are on opposite sides of the plane. The oscillation model is shown to account satisfactorily for the phenomena of substitution and to allow the construction of symmetrical formulæ for naphthalene, anthracene, phenanthrene, and pyrene, whilst it also accounts for the difference in properties between benzene and *cyclooctatetraene*; it leads to a uniform formulation of *p*-quinones and quinols, and accounts for the existence of two forms of *o*-quinones. Triphenylmethyl and the metallic ketyls can be formulated without recourse to tervalent carbon, whilst the phenomena of hydrogenation of the phthalic acids are also explained. For details, the original paper must be consulted.

H. W.

The Melting Points, Refractive Indices and Densities of a Series of Dihalogenobenzenes. J. NARBUTT (*Ber.*, 1919, 52, [B], 1028—1034).—The melting points were determined by observation of the cooling curves of the molten substances, and are accurate to within $\pm 0.02^\circ$ for m. p.'s above the atmospheric temperature and to within $\pm 0.1^\circ$ for those of lower temperature; the error in the case of the refractive indices, determined with an Abbé refractometer, does not exceed $\pm 0.0002-3$, whilst the densities are accurate to $\pm 0.0001-2$. The following constants have been determined: *p*-dichlorobenzene, m. p. 52.9° ; *o*-dichlorobenzene, m. p. -17.5° , D_4^{15} 1.3104, D_4^{20} 1.3048, n_D^{15} 1.5524; *m*-dichlorobenzene, m. p. -24.4° , D_4^{15} 1.2937, D_4^{20} 1.2881, n_D^{15} 1.5472; *p*-chlorobromobenzene, m. p. 64.6° ; *o*-chlorobromobenzene, m. p. -12.6° , D_4^{15} 1.6511, D_4^{20} 1.6444, n_D^{15} 1.5821; *m*-chlorobromobenzene, m. p. -21.2° , D_4^{15} 1.6365, D_4^{20} 1.6297, n_D^{15} 1.5773; *p*-dibromobenzene, m. p. 86.9° ; *o*-dibromobenzene, m. p. $+1.8^\circ$, D_4^{15} 1.9633, D_4^{20} 1.9557, n_D^{15} 1.6117; *m*-dibromobenzene, m. p. -6.9° , D_4^{15} 1.9599, D_4^{20} 1.9523, n_D^{15} 1.6083; *p*-bromiodobenzene, m. p. 90.1° ; *o*-bromiodobenzene, m. p. $+2.1^\circ$; *m*-bromiodobenzene, m. p. -9.3° ; *p*-diiodobenzene, m. p. 129.0° ; *o*-diiodobenzene, m. p. 23.4° ; *m*-diiodobenzene, m. p. 34.2° . H. W.

Products of Nitration of *p*-Cymene. OSSIAN ASCHAN [with TERÄSVUORI and PER EKWALL] (*Finska Kem. Medd.*, 1918, 5 pp.; from *Chem. Zentr.*, 1919, i, 227).—Direct nitration of cymene

yielded 2-nitrocymene, D_4^{20} 1.067, in minimal amount. Cymene was also gradually added to well-cooled concentrated nitric acid (D 1.52), and the following substances were isolated by prolonged fractional crystallisation of the solidified product. I. *Substance*, $C_{18}H_{17}O_{10}N_5$, yellow needles, m. p. 70° , which when reduced with ammonium sulphide yielded an *amine*, orange needles, m. p. $77-78^\circ$ (*hydrochloride*, m. p. $215-218^\circ$). II. 3:5-Dinitro-*p-cymene*, greenish-white plates, m. p. 54° , which were reduced to *nitro-carvacrylamine*, yellow needles or prisms, m. p. $80-82^\circ$ (*hydrochloride*, pale red crystals, m. p. $208-210^\circ$; *acetyl derivative*, m. p. 111°). *Nitrocarvacrol*, needles, m. p. $116-117^\circ$, was formed as by-product during diazotisation. III. *Substance*, $C_{10}H_{12}O_5N_2$, probably dinitrohydroxy-*p-cymene*, $C_6H_2Me(NO_2)_2 \cdot CMe_2 \cdot OH$, prisms or plates, m. p. $90-91^\circ$.
H. W.

The Dimethylnaphthalenes of Coal Tar. R. WEISSGERBER and O. KRUBER (*Ber.*, 1919, 52, [B], 346-370).—Physical methods for the separation of the dimethylnaphthalenes in the heavy-oil fraction, b. p. $260-265^\circ$, seem to be out of the question, and when it is considered how many sulphonic acids could be formed by the ten possible isomerides, no great help could be expected from the sulphonation method which has served so well in the case of the polymethylbenzenes. Nevertheless, the authors have tried the method, and by varying the conditions have succeeded in isolating the 1:6-, 2:6-, and 2:7-isomerides with far less trouble than was anticipated.

1:6-DIMETHYLNAPHTHALENE.—The crude oil is purified by alternate fractionation and agitation with small quantities of concentrated sulphuric acid in the cold. It is then stirred with 60% of its weight of 98% sulphuric acid for eight to ten hours at about 40° , when the pasty mass of sulphonic acids is separated and mixed with a little water. A solid *sulphonic acid* is deposited, which is purified by crystallisation from 33% sulphuric acid and converted into its *sodium salt*, bundles of needles, $1H_2O$, and *amide*, $C_{12}H_{13}O_2NS$, m. p. 185° . The sulphonic acid is hydrolysed by means of steam at $130-140^\circ$ to 1:6-dimethylnaphthalene, which has b. p. $262-263^\circ$, D^{15} 1.0056 (α -methylnaphthalene has D^{15} 1.0267), and forms a *picrate*, long, orange-red needles, m. p. 114° . The constitution of the hydrocarbon is revealed by the following series of reactions.

By the alkaline fusion of the sulphonate, 4:7-dimethyl- α -naphthol is obtained, in slender needles, m. p. 82° , which couples with benzenediazonium chloride to form a *dye*, $C_{18}H_{16}ON_2$, dark red leaflets, m. p. 134° , which is insoluble in, and indifferent to, potassium hydroxide, and is therefore an *o*-hydroxyazo-compound. On oxidation with chromic acid in glacial acetic acid, the hydrocarbon yields 2:5-dimethyl- α -naphthaquinone, which crystallises in pale yellow rosettes of pungent-smelling needles, m. p. 95° , and may be oxidised further, by permanganate, to 3-methyl-*o*-phthalic acid (Jürgens, A., 1907, i, 1036). The production of the *o*-azo-dye, the

p-quinone, and the 3-methylphthalic acid indicates that the hydrocarbon is either a 1:6- or 1:7-dimethylnaphthalene and the sulphonic acid the 4-derivative. For the final decision, oxidation to a dicarboxylic acid is necessary, but many methods were tried before this could be accomplished. Oxidation with alkaline ferricyanide gives *naphthalene-1:6-dicarboxylic acid*, which crystallises in microscopic needles, m. p. 310°, and forms a *methyl* ester, rosettes of needles, m. p. 99°. Prolonged boiling with about 5% nitric acid, however, gives chiefly *6-methyl- α -naphthoic acid*, which crystallises in slender, white needles, m. p. 150—152°, forms a *methyl* ester, a pale yellow oil with a resinous odour, b. p. 183—187°/30 mm., and an *ethyl* ester, b. p. 203—205°/30 mm., and yields β -methylnaphthalene when heated with hydrochloric acid at 222—230°.

The above dicarboxylic acid was also prepared as follows: β -Naphthylamine-5-sulphonic acid is diazotised and boiled with cuprous cyanide, the *potassium 6-cyanonaphthalene-1-sulphonate* is distilled with potassium cyanide, and the 1:6-dicyanonaphthalene (short needles, m. p. 208—210°; compare Darmstädter and Wichelhaus, *Annalen*, 1869, 152, 309) is hydrolysed.

2:6-DIMETHYLNAPHTHALENE.—If the sulphonation is carried out at 135—140°, and the product is poured on ice, a much less soluble *sulphonic acid* soon crystallises. This crystallises in large, glistening leaflets, gives a sparingly soluble *sodium* salt, 5H₂O, and an *amide*, m. p. 265—266°, and yields the known 2:6-dimethylnaphthalene on hydrolysis. The hydrocarbon has m. p. 110—111°, b. p. 261—262°, and has the odour of aniseed, whereas the specimen obtained by Baeyer and Villiger from ionone (A., 1899, i, 922) had the odour of orange blossom. The identity of the compound is established, however, by its oxidation with chromic acid to 2:6-dimethylnaphtha-1:4-quinone and then by permanganate to trimellitic acid (*ibid.*).

The explanation of the different course of the sulphonation was found by sulphonating the pure hydrocarbons. 1:6-Dimethylnaphthalene yields the 4-sulphonic acid in the cold, but a mixture of freely soluble acids at above 100°; 2:6-dimethylnaphthalene yields the freely soluble 8-sulphonic acid in the cold, which is hydrolysed to the hydrocarbon by boiling with about 70% sulphuric acid, and converted into the 7-sulphonic acid by heating with 78% sulphuric acid at 135—140°. The constitution of the sulphonic acids follows from the properties of the corresponding naphthols. 2:6-Dimethylnaphthalene-8-sulphonic acid [*3:7-dimethyl- α -naphthalenesulphonic acid*] crystallises in flat needles and tablets, its *chloride* in stout prisms, m. p. 105—107°, and its *amide* in rosettes of leaflets, m. p. 207°. The product of the alkaline fusion, 3:7-dimethyl- α -naphthol, forms colourless needles, m. p. 105—106°, and couples with benzenediazonium chloride to give *bisbenzeneazo-3:7-dimethyl- α -naphthol*, C₂₄H₂₀ON₄, in steel-blue needles, m. p. 191°. 3:7-Dimethyl- β -naphthalenesulphonic acid, the above product of the sulphonation at 135—140°, gives rise to 3:7-dimethyl- β -naphthol, which crystallises in glistening needles, m. p. 173—174°.

and forms a *benzeneazo*-compound, in brilliant orange-red needles, m. p. 149—151°. This is converted into 3:7-*dimethylnaphtha*-1:2-*quinone*, ruby-red needles, m. p. 151—152°, by reduction to the aminonaphthol, followed by oxidation with dichromate. 2:6-Dimethylnaphtha-1:4-*quinone* (above) reacts with phenylhydrazine to form 4-*benzeneazo*-2:6-*dimethyl- α -naphthol*, which crystallises in fiery orange-red needles, m. p. 240—241° (decomp.), and changes in alcoholic solution from orange to magenta on the addition of alkali hydroxide.

2:7-DIMETHYLNAPHTHALENE.—For practical purposes, it is not advisable to isolate the 2:6-isomeride from the original oil, but to proceed as follows: the oil is sulphonated in the cold, and the liquid sulphonic acids removed from the solid 1:6-dimethylnaphthalenesulphonic acid are heated at 150—160° for a few hours and then hydrolysed, giving a mixture of solid and liquid hydrocarbons. The solid mixture generally has m. p. 50—60°, but is frequently so rich in the 2:6-isomeride as to yield this readily by fractional crystallisation. If not, it is sulphonated at 135—140°, the solid 2:6-dimethylnaphthalenesulphonic acid is removed, and the liquid acids hydrolysed again. Once more a mixture of solid hydrocarbons with low m. p. is obtained. This is then sulphonated at about 40°, and the pasty product crystallised from 30% sulphuric acid. Two sulphonic acids separate, which are hydrolysed in the usual way, when 2:7-*dimethylnaphthalene* is obtained in glistening leaflets with an aromatic odour, m. p. 96—97°, b. p. 262°, the *picrate* crystallising in pale yellow needles, m. p. 135—136°.

The constitution of the new hydrocarbon is established in the usual way. When sulphonated at 100°, it yields 2:7-*dimethylnaphthalene*-3-sulphonic acid, which crystallises in pearly, sword-like forms, and forms a *sodium* salt, bundles of needles, and an *amide*, m. p. 197—198°. The sodium salt can also be isolated from the above crude mixture obtained by sulphonating in the cold, or from the mother liquors of the above 2:6-dimethylnaphthalenesulphonate. When fused with potassium hydroxide, the salt yields 3:6-*dimethyl- β -naphthol*, in lanceolate crystals, m. p. 171—172°, which gives a brilliant orange-red *benzeneazo*-dye, m. p. 183—184°. When the dye is reduced and the white amine is oxidised by chromic acid, 3:6-*dimethylnaphtha*-1:2-*quinone* is obtained, in stout, brownish-red prisms, m. p. 152—153°. The isomeric 3:6-*dimethylnaphtha*-1:4-*quinone*, yellow needles, m. p. 114—115°, is obtained by oxidising the hydrocarbon with chromic acid, and it yields trimellitic acid on oxidation with permanganate.

The coal-tar fraction, b. p. 220—290°, is commonly regarded as being poor in solid ingredients, in fact, is often used to maintain other fractions in the liquid state. The discovery of two solid dimethylnaphthalenes is therefore contrary to this idea. The only genuine oils in the fraction are the β -methyl- and 1:6-dimethylnaphthalenes, the fluidity being due to the enormous depression of the freezing point mutually exerted by the ingredients. A

possible outlet for naphthalene as an oil would therefore consist in methylating it.

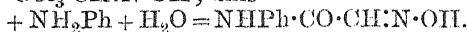
J. C. W.

2:3-Dimethylnaphthalene in Coal Tar. R. WEISSGERBER (*Ber.*, 1919, 52, [B], 370—371).—On working up the liquid sulphonic acids accompanying the 2:6-dimethylnaphthalene-sulphonic acid (preceding abstract), a well-defined sodium salt was once accidentally obtained which gave a fourth dimethylnaphthalene, crystallising in large leaflets, m. p. 104—105°. By direct comparison, this has now been identified with the 2:3-dimethylnaphthalene (guaiene) recently obtained by Schroeter and others from guaiacum resin (this vol., i, 84).

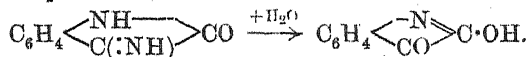
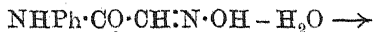
J. C. W.

Oximinoacetanilides and their Condensation to Isatins.

T. SANDMEYER (*Helv. Chim. Acta*, 1919, 2, 234—242).—If a freshly prepared solution of hydroxylamine sulphate is boiled with aniline or many of its derivatives and chloral hydrate, oximinoacetanilides are formed, according to the equations: $\text{CCl}_3\cdot\text{CHO} + \text{NH}_2\cdot\text{OH} \rightarrow \text{CCl}_3\cdot\text{CH:N}\cdot\text{OH}$; this



The majority of these compounds, if the ortho-position is unoccupied, give excellent yields of isatins when heated with sulphuric acid at temperatures varying from 55° to 100° and then diluted with water; thus:



The solution of hydroxylamine sulphate is obtained by boiling one of hydroxylaminesulphonic acid, prepared by Raschig's method. The oximinoacetanilides are all more or less pale yellow, flocculent, crystalline precipitates. The following have been prepared: *oximinoacet-anilide*, m. p. 175°; -o-, -m-, and -p-*toluidides*, m. p.'s 121°, 146°, 162° respectively; -m- and -p-*xylyldides*, m. p.'s 161° and 151°; -o-*anisidide*, m. p. 140°; -p-*phenetidide*, m. p. 195°; -*methyl*-, -*ethyl*-, and -*benzyl-anilides*, m. p.'s 145°, 160°, and 142°; -o-, -m-, and -p-*chloroanilides*, m. p.'s 150°, 154°, 165°; -2:5-, -3:4-, and -3:5-*dichloroanilides*, m. p.'s 163°, 158°, 185°; -5- and -4-*chloro-o-toluidides*, m. p.'s 167°, 148°; -6- and -4-*chloro-m-toluidides*, m. p.'s 187°, 134°; -2- and -3-*chloro-p-toluidides*, m. p.'s 177°, 188°; -4-*chloro-o-anisidide*, m. p. 182°; -p-*bromoanilide*, m. p. 167°; -2:4-*dibromoanilide*, m. p. 215°; and *oximinoacetanthranilic acid*, m. p. 208°.

The following isatins are new: 4:7-*dimethylisatin*, orange-yellow, m. p. 250°; 7-*chloroisatin*, reddish-brown, m. p. 175°; 4:6-*dichloroisatin*, lemon-yellow, m. p. 250°; 4-*chloro-7-methylisatin*, orange-yellow, m. p. 273°; 5-*chloro-7-methylisatin*, yellowish-brown, m. p. 265°; 7-*chloro-4-methylisatin*, orange-yellow, m. p. 252°; 4-*chloro-7-methoxyisatin*, dark red, m. p. 240°; and *isatin-7-carboxylic acid*, brownish-yellow, m. p. 235°.

J. C. W.

The Conception of Internal Molecular Strain and the Theory of Benzene. D. VORLÄNDER (*Ber.*, 1919, 52, [B], 263—283).—A theoretical paper dealing chiefly with the problems of orientation in the benzene series.

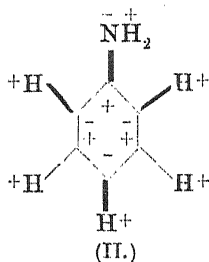
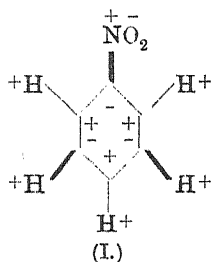
I. *Positive and Negative Radicles attached to the Benzene Nucleus.*—The various radicles are sharply divided into two classes, according to the position occupied by the second substituent in bromination, nitration, or sulphonation. One group exerts a *positive* influence, directing the new substituent into the *meta*-position, and includes $\cdot\text{SO}_3\text{H}$, $\cdot\text{NO}_2$, $\cdot\text{CHO}$, $\cdot\text{CH}\cdot\text{NO}_2\text{H}$, $\cdot\text{CO}_2\text{H}$, $\cdot\text{CO}_2\text{Alk}$, $\cdot\text{CO}\cdot\text{NH}_2$, $\cdot\text{COAlk}$, $\cdot\text{CO}\cdot\text{CO}_2\text{H}$, $\cdot\text{C}\cdot\text{OH}$, $\cdot\text{CN}$, $\cdot\text{CCl}_3$, $\cdot\text{NH}_3\text{X}$, $\cdot\text{NH}_2\text{Alk}\cdot\text{X}$, $\cdot\text{NHAlk}_2\text{X}$, $\cdot\text{NAlk}_3\text{X}$, $\cdot\text{NH}_2\text{AcylX}$. The other group has a *negative* influence, and is *ortho*-*para* orienting; it includes halogens, $\cdot\text{OH}$, $\cdot\text{OAlk}$, $\cdot\text{OAcyl}$, $\cdot\text{NH}_2$, $\cdot\text{NHAlk}$, $\cdot\text{NAlk}_2$, $\cdot\text{NHAcyl}$, $\cdot\text{N}\cdot\text{N}\cdot$, $\cdot\text{CH}_3$, $\cdot\text{CH}_2\text{Alk}$, $\cdot\text{CHAlk}_2$, $\cdot\text{CMe}_3$, $\cdot\text{CH}_2\text{Cl}$, $\cdot\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$, $\cdot\text{CH}_2\cdot\text{SO}_3\text{H}$, $\cdot\text{CH}_2\cdot\text{NH}_2$, $\cdot\text{CH}_2\cdot\text{CN}$, $\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, $\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$, $\cdot\text{C}\cdot\text{C}\cdot\text{CO}_2\text{H}$, $\cdot\text{C}_6\text{H}_5$. At first sight, it would seem to be a novel conception to regard the groups $\cdot\text{SO}_3\text{H}$, $\cdot\text{CO}_2\text{H}$, and $\cdot\text{NR}_3\text{X}$ as positive and $\cdot\text{NH}_2$ as negative, and to find a difference between $\cdot\text{COME}$ on the one hand and $\cdot\text{OMe}$ and $\cdot\text{CH}_3$ on the other, but the author's notion is not based on any valency theories at all. The terms + and - are used to express the kind of antithesis or strain between the connected atoms. Thus, in any member of the above positive series, the atom which is attached to the benzene ring is positive; for example, $\text{Ph}\cdot\overset{+}{\text{NR}_3}\cdot\overset{+}{\text{OH}}$, $\text{Ph}\cdot\overset{+}{\text{NO}_2}$, $\text{Ph}\cdot\overset{+}{\text{COR}}$, $\text{Ph}\cdot\overset{+}{\text{SO}_2}\cdot\overset{+}{\text{OH}}$, $\text{Ph}\cdot\overset{+}{\text{CO}}\cdot\overset{+}{\text{OH}}$. In the negative series, the connecting atom is negative, thus: $\text{Ph}\cdot\overset{-}{\text{OCH}_3}$, $\text{Ph}\cdot\overset{-}{\text{CH}_3}$, $\text{Ph}\cdot\overset{-}{\text{NH}_2}$, $\text{Ph}\cdot\overset{-}{\text{OH}}$.

II. *The Nature of the Ammonium Salt Group, $\cdot\text{NR}_3\text{X}$.*—In the following abstract it is shown that aromatic quaternary ammonium salts are difficult to brominate or nitrate, but that the second substituent goes to the *meta*-position. The group $\cdot\text{NR}_3\text{X}$ therefore resembles the $\cdot\text{NO}_2$ group. This is interesting in view of the fact that anilines and their alkyl and acyl derivatives, which give *ortho*- and *para*-derivatives when brominated or nitrated in acetic acid solution, yield *meta*-compounds if dissolved in an excess of concentrated sulphuric acid, for then they are acting as ammonium salts. Like the $\cdot\text{CO}$, $\cdot\text{NO}_2$, and $\cdot\text{CN}$ groups, also, the $\cdot\text{NR}_3\text{X}$ group protects the benzene nucleus against oxidation and coupling; for example, when *o*-tolyltrimethylammonium sulphate is oxidised, it merely gives *o*-benzobetaine (this vol., i, 262). Unlike these groups, however, the $\cdot\text{NR}_3\text{X}$ radicle has no chromophoric properties, in spite of the fact that the production of perbromides, etc., shows it to be somewhat unsaturated.

III. *Nitration of Benzotrichloride and tert.-Butylbenzene.*—Under conditions which preclude the hydrolysis of benzotrichloride, nitration gives a *meta*-compound (this vol., i, 263). This illustrates the difference between the $\cdot\text{CH}_3$ group, in which the

carbon is $-$, and the $\cdot\text{CCl}_3$ group, in which it is $+$. *tert.*-Butylbenzene, on the other hand, gives almost entirely a *p*-nitro-derivative (this vol., i, 261). It is very difficult to chlorinate or oxidise, there being apparently a steric hindrance against the occupation of the ortho-position.

IV. *The Benzene Theory* (compare A., 1902, ii, 250).—The carbon atoms in the benzene ring are also written alternately $+$ and $-$. If the ring bears a positive substituent like $\cdot\text{NO}_2$, the formula may be expressed as in (I), if a negative substituent like $\cdot\text{NH}_2$, as in (II), in which the strong lines represent greater, and the weak lines lesser, tensions.



This conception helps to explain why compounds of the first type are more stable than the others, and why the first give meta-derivatives with halogen or nitric and sulphuric acids, whilst the second give ortho- and para-compounds. Other problems are discussed along the same lines, including the position occupied by a third substituent when (*a*) two positive, (*b*) two negative, and (*c*) one positive and one negative substituents are already present.

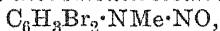
J. C. W.

Bromination and Nitration of Aromatic Quaternary Ammonium Salts. D. VORLÄNDER and ERNST SIEBERT (*Ber.*, 1919, 52, [B], 283—307).—I. *Bromination of Phenyltrimethylammonium Bromide*.—This salt is prepared as follows: dimethylaniline is warmed with methyl sulphate and benzene, the hygroscopic product, $\text{NMe}_2\text{Ph}\cdot\text{SO}_4\text{Me}$, m. p. 71 — 92° (Ullmann, A., 1903, i, 394), is dissolved in 20% hydrobromic acid and treated with bromine, and the tribromide so formed (Tafel, A., 1898, i, 519) is boiled with water and the solution evaporated. Phenyltrimethylammonium bromide forms colourless crystals, m. p. 214° , and the corresponding picrate has m. p. 115° . Tafel did not succeed in brominating the salt (A., 1898, i, 471), but it is now found that reaction with bromine takes place at 70° in the presence of iron powder, the product being *m*-bromophenyltrimethylammonium bromide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NMe}_3\text{Br}$. This crystallises in stout prisms, m. p. 236 — 238° (decomp.), combines with bromine to form an orange-red tribromide, m. p. 93 — 95° , and a yellow dibromide, m. p. 120 — 122° , and may be converted into the corresponding iodide, colourless prisms, m. p. 202° (Wurster and Scheibe, A., 1879,

107), *tri-iodide*, dark brown leaflets, m. p. 110°, and yellow *picrate*, m. p. 151°. The iodide decomposes at 165°/13 mm. into *m*-bromodimethylaniline (*ibid.*), which has m. p. 9–10°, b. p. 125°/10 mm., 253–254°/atm., and is characterised by its *picrate*, hexagonal tablets or prisms, m. p. 134–138°, and by conversion into *m*-bromo-*p*-nitrosodimethylaniline, brownish-green needles, m. p. 116° (not 148° as given by Wurster and Scheibe).

If the bromination is carried out at 100–120°, the product is 3:4-dibromophenyltrimethylammonium bromide, which crystallises as a mass of minute filaments, m. p. 180° (decomp.). The corresponding tribromide, $C_6H_3Br_3 \cdot NMe_3 \cdot Br_3$, forms golden-yellow leaflets, m. p. 147–149° (decomp.); the iodide crystallises in almost white, glistening needles, m. p. 185° (decomp.), and the *tri-iodide* forms brown leaflets, m. p. 136–138°. If the iodide is converted into the hydroxide, and this is distilled under reduced pressure, 3:4-dibromodimethylaniline is formed. This crystallises in needles or hexagonal tablets, m. p. 68–70°, decomposes into a reddish-violet dye on distillation under ordinary pressures, and may also be obtained by brominating 3-bromodimethylaniline or methylating 3:4-dibromoaniline. The base forms a characteristic *picrate*, flat, yellow needles, m. p. 142–146°, and a *perbromide*, m. p. 161–163° (decomp.), yields a mixture of products when treated with nitrous acid, including a golden-yellow *nitro*-compound, m. p. 131°, and may be converted into the above 3:4-dibromophenyltrimethylammonium salts after treatment with methyl sulphate.

For the sake of comparison, the unknown 3:5- and 3:6-dibromodimethylanilines have been prepared from the corresponding anilines by means of methyl sulphate. 3:5-Dibromodimethylaniline crystallises in large, white tablets, m. p. 77–79°, and forms a *picrate*, m. p. 151–153°, and 3:5-dibromophenyltrimethylammonium tribromide may be precipitated by means of bromine and hydrobromic acid from the alkaline mother liquor obtained in the preparation as yellow leaflets, m. p. 149° (decomp.). 3:6-Dibromodimethylaniline has m. p. below –35°, b. p. 134–137°/10 mm., forms a pale yellow *picrate*, m. p. 149°, and reacts with nitrous acid to give 3:6-dibromonitrosomethylaniline,



in small, white needles, m. p. 86–87°. 3:6-Dibromophenyltrimethylammonium tribromide forms golden-yellow leaflets, m. p. 135–136° (decomp.).

II. Nitration of Phenyltrimethylammonium Nitrate.—The bromide is converted into the nitrate, m. p. 110–115°, by evaporating two or three times with dilute nitric acid. Nitration takes place when the salt is heated at 100° with fuming nitric acid for eight hours, the product being *m*-nitrophenyltrimethylammonium nitrate, which crystallises in colourless prisms, m. p. 220–240° (decomp.) (compare Tafel, *loc. cit.*). The corresponding *picrate* forms yellow tablets, m. p. 151–153°, the *iodide* hexagonal or quadratic tablets, decomp. 205°, and the *tri-iodide* dark brown

leaflets, m. p. 143—145° (decomp.). The iodide yields *m*-nitrodimethylaniline, m. p. 58—60°, when heated in a vacuum, the product being identical with one made by Ullmann's method (A., 1900, i, 619). The action of sodium nitrite on hydrochloric acid solutions of this base leads to different products, according to the concentration of the acid. In dilute acid, the product is *m*-nitro-nitrosomethylaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NO}$, m. p. 76° (Noelting and Stricker, A., 1886, 544); from more concentrated solutions (acid with D 1.1—1.2), the products also include 3:4- and 3:6-dinitrodimethylanilines, m. p.'s 174—175° and 112° respectively.

III. *Nitration of o-Tolyltrimethylammonium Nitrate*.—Dimethyl-*o*-toluidine is methylated by means of methyl sulphate, the product is converted into the ammonium tribromide, and this is heated with dilute nitric acid. *o*-Tolyltrimethylammonium nitrate crystallises in quadratic leaflets, m. p. 175°; the corresponding *picrate* has m. p. 112—114°, the *mercurichloride* m. p. 192° (decomp.), and the *aurichloride* m. p. 189°. The nitrate readily reacts with boiling nitric acid (D 1.51) to form 5-nitro-*o*-tolyltrimethylammonium nitrate, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_3 \cdot \text{NO}_3$, in flat needles, m. p. 230—235° (decomp.), which behave in a remarkable manner towards alkalis. When covered with 33% potassium hydroxide, the salt becomes bluish-green and then deep indigo-blue, changing to a reddish-violet solution on dilution, which gradually deposits brownish-red or green flocks. The corresponding *picrate* forms long, yellow needles, m. p. 202°, the *mercurichloride* long, white needles, m. p. 226° (decomp.), the *aurichloride* yellow leaflets, m. p. 200° (decomp.), the *platinichloride* orange-red needles and prisms, m. p. 233° (decomp.), and the *iodide* golden-yellow needles, m. p. 195° (decomp.). The iodide decomposes when heated in a vacuum into 4-nitrodimethyl-*o*-toluidine, $\text{NO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2$, m. p. 13.5—15°, b. p. 160°/16 mm.; hydrochloride, m. p. 197° (decomp.) (compare Gnehm and Blumer, A., 1899, i, 266). When the ammonium hydroxide is evaporated in a flask and then heated, trimethylamine, formaldehyde, and other gases are evolved, and at 170—180°/15—30 mm., *m*-nitrodimethylaniline distils into the receiver.

IV. *Nitration of m-Tolyltrimethylammonium Nitrate*.—*m*-Toluidine is converted in the above manner into *m*-tolyltrimethylammonium nitrate, which forms prismatic crystals, m. p. 134°, the corresponding *picrate* having m. p. 108°. When boiled with fuming nitric acid, the salt yields 4-nitro-*m*-tolyltrimethylammonium nitrate, white tablets, m. p. 195° (decomp.), the corresponding *picrate* having m. p. 205°, the *iodide*, m. p. 165° (decomp.), and the *tri-iodide*, crystallising in violet-brown needles, m. p. 140°. The iodide decomposes at 210°/11 mm. into 6-nitrodimethyl-*m*-toluidine, which crystallises in dark yellow, flat, triclinic needles, m. p. 83°. This has been prepared also by methylating 6-nitro-*m*-toluidine (made from *m*-toluidine or *m*-cresol), and it corresponds with a nitrodimethyl-*m*-toluidine described by Wurster and Riedel (A., 1880, 109).

V. *Nitration of p-Tolyltrimethylammonium Nitrate*.—Dimethyl-*p*-toluidine is converted into *p*-tolyltrimethylammonium tribromide, golden-yellow leaflets, m. p. 113—115°, and then into the *nitrate*, white leaflets, m. p. 125°, and *picrate*, long, yellow needles, m. p. 195—197°, by the usual means. 3-Nitro-*p*-tolylammonium *nitrate* crystallises in glistening, white scales, m. p. 205—220° (decomp.), the *picrate* in long, yellow needles, m. p. 203°, the *tribromide* in long, yellow prisms, m. p. 152° (decomp.), the *iodide* in pale yellow prisms, m. p. 195° (decomp.), the *tri-iodide* in violet-brown prisms, m. p. 126°, and the *platinichloride* forms orange-yellow crystals, m. p. 207° (decomp.), and the *mercurichloride* long, white, prismatic needles, m. p. 141°. The iodide decomposes at 160°/12 mm. into 2-nitrodimethyl-*p*-toluidine, yellowish-red plates, m. p. 38°, the *picrate* having m. p. 147°. The base reacts with nitrous acid to form 2-nitrosodimethyl-*p*-toluidine, m. p. 57—59° (Pinnow, A., 1896, i, 161), and it may be obtained by methylating 2-nitro-*p*-toluidine or nitrating dimethyl-*p*-toluidine (Haibach, A., 1902, i, 444; D.R.-P. 69188).
J. C. W.

Oxidation of Secondary and Tertiary Aromatic Amines.

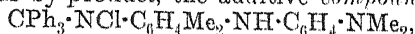
XX. Ditertiary Hydrazines and Related Substances.

HEINRICH WIELAND (*Ber.*, 1919, 52, [B], 886—893).—Although the explanation of the mechanism of the blue colour reaction of diphenylamine advanced by Kehrman and Micewicz (A., 1912, i, 1020), and Wieland (A., 1913, i, 1386), has been generally accepted, certain details have been criticised by Marquoyrol and Muraour (A., 1914, i, 577). Thus, the removal of the imino-hydrogen atom by oxidation of the free base has been attributed by Wieland to the unsaturated nature of tervalent nitrogen; when this becomes saturated, as by salt formation, the oxidising agent appears to attack the benzene nucleus. Under similar conditions, however, the French chemists found diphenylamine to be apparently less readily oxidised in concentrated than in dilute acid solution; this is now shown to be due, however, to the consumption of the oxidising agent by side-reactions caused by the concentrated acid.

Diphenylmethylaniline is readily oxidised to a carmine-red dye, which is reduced to NN'-diphenyl-NN'-dimethylbenzidine, colourless, silky needles, m. p. 171°. Diphenylmethylanilinesulphonic acid is formed as a by-product of the methylation of diphenylamine with methyl sulphate; the sodium salt was analysed. The mechanism of the oxidation of salts of tertiary amines is also discussed, and it is suggested that the first stage of the process consists in the removal of the hydrogen atoms introduced with the acid, and that this is followed by oxidation of the *para*-hydrogen atoms; the first phase is then analogous to the formation of dianthrone from anthranol. The explanation is not, however, valid for triphenylamine, for which the primary addition of oxygen or hydroxyl is assumed.
H. W.

Ditertiary Hydrazines. XXI. Chlorotriarylmethanes and Diarylamines. HEINRICH WIELAND, BORIS DOLGOW, and TALBOT J. ALBERT (*Ber.*, 1919, **52**, [B], 893—898).—It has been previously shown that the dissociation products of ditertiary hydrazines unite with triphenylmethyl to yield triphenylmethyldiarylamines; attempts are now described to obtain these substances by the action of chlorotriphenylmethane on diarylamines. In general, however, derivatives of tetraphenylmethane are obtained, the formation of which is due to the transformation of the triarylmethyldiarylamines under the experimental conditions adopted: $\text{CPh}_3 \cdot \text{NPh}_2 \rightarrow \text{CPh}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{NHPh}$.

p-Anilinotetraphenylmethane, slender needles, m. p. 242° , after previous softening, is prepared by heating triphenylmethyl chloride and diphenylamine in benzene solution; it is oxidised by chromic acid in glacial acetic acid solution to a benzidine dye, and yields a tribromo-derivative, m. p. 214 — 215° . It can also be prepared by heating *N*-triphenylmethyldiphenylamine with diphenylamine hydrochloride in the presence of benzene, or by protracted heating of the first-named substance in glacial acetic acid solution. The action of chlorotriphenylmethane on *p*-ditolylamine, or the transformation of *N*-triphenylmethylditolylamine, leads to the formation of a substance, m. p. 217 — 218° , which probably has the constitution $\text{CHPh}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{C}_6\text{H}_4\text{Me})_2$. A similarly constituted compound, slender, colourless needles, m. p. 197 — 199° , is obtained from chlorotriphenylmethane and *p*-dianisylamine. Reaction between *p*-tetramethyldiaminodiphenylamine and chlorotriphenylmethane is of particular interest, since, in this instance, the primary product can be isolated, and is identical in all respects with that obtained from triphenylmethyl and the radicle $\text{N}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ (Wieland, A., 1915, i, 848); as by-product, the additive compound,



is formed, which decomposes into indamine and triphenylmethane.

H. W.

The Nitro-derivatives of Phenyl- β -naphthylamine. HUGH RYAN and JAMES J. DRUMM (*Proc. Roy. Irish Acad.*, 1918, **34**, [B], (8), 165—174).—Amongst the compounds proposed for use as stabilisers for nitrocellulose powders is phenylaceto- β -naphthalide. The nature of its action has not hitherto been investigated. Since it seemed likely that the stabilising action is due to its power of combining with nitrous and nitric acids, its reaction with these substances was examined.

Nitrogen peroxide, from lead nitrate, has apparently no action on phenylaceto- β -naphthalide in dry ethereal solution. In presence of moist ether, hydrolysis and nitration occur. Phenyl- β -naphthylamine and a mononitrophenyl- β -naphthylamine, colourless, cubical crystals from xylene, m. p. 119 — 120° , are formed. The orientation of the mononitro-derivative was not determined. It was also obtained from the stabiliser and cold concentrated nitric acid.

In alcoholic solution, the stabiliser slowly forms two trinitro-compounds, m. p. 242° and 179° respectively. The same compounds are produced when a mixture of amyl nitrite, nitric acid (1—6 molecules), and the stabiliser in glacial acetic acid is allowed to remain. Under similar conditions, in the absence of amyl nitrite, no action occurs. The trinitro-compound, m. p. 179° , is also obtained when phenyl- β -naphthylamine in glacial acetic acid is treated with a large excess of nitric acid. It forms orange crystals from glacial acetic acid. The yellow trinitro-compound, m. p. 242° , is also formed when phenyl- β -naphthylnitrosoamine reacts with nitric acid in glacial acetic acid, and is identical with 2':4'-dinitrophenyl-1-nitro-2-naphthylamine, which was prepared by Goldberg's method (A., 1908, i, 288) from chloro-2:4-dinitrobenzene and 1-nitro-2-naphthylamine.

The authors have also prepared the following substances by the Goldberg reaction in hot nitrobenzene:

p-Nitrophenyl- β -naphthylamine (from β -naphthylamine and *p*-bromonitrobenzene) forms yellow, matted, acicular crystals from benzene, m. p. 283 — 284° , which give a bluish-violet coloration with concentrated sulphuric acid.

Phenyl-1-nitro- β -naphthylamine (from bromobenzene and 1-nitro- β -naphthylamine) forms deep red prisms from alcohol, m. p. 105 — 106° . Its solution in cold sulphuric acid has a deep red colour.

1-Chloro-2:4-dinitrobenzene and β -naphthylamine yield a compound, red prisms, m. p. 170 — 171° . Other compounds prepared in the course of this work are: a trinitro-derivative of phenyl- β -naphthylamine, melting and decomposing at 210° , and a dinitro-derivative, brown prisms, melting and decomposing at 170 — 180° .

F. C.

Improvements in the Manufacture of Nitrophenols.

DAVID BAIRD MACDONALD and JACKSON CALVERT (Brit. Pat., 126062 and 126084).—The formation of 2:4-dinitrophenol in the nitration of benzene with nitric acid in presence of mercuric nitrate is greatly facilitated by passing carbon dioxide either into the reaction mixture or through the benzene or nitric acid contained in a separate vessel, the mixed vapours then being led into the mixture of nitric acid and mercuric nitrate in the former case, or of benzene and mercuric nitrate, together with a small portion of the nitric acid, in the latter. The reaction is allowed to proceed for about six hours at 40 — 50° , and commercially pure dinitrophenol may be isolated from the reaction mixture by simply volatilising the more volatile constituents.

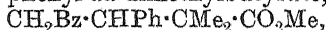
According to the second patent, air or oxygen, or a mixture of air and oxygen with or without carbon dioxide, may be substituted for the carbon dioxide there employed with similar results. [See, further, *J. Soc. Chem. Ind.*, 1919, 406A.]

G. F. M.

Pinabietic Acid, a Resin Acid from the Sulphate Cellulose Liquors. OSSIAN ASCHAN and K. E. EKHOLM (*Finska Kem. Medd.*, 1918, pp. 8; from *Chem. Zentr.*, 1919, i, 285—286).—*Pinabietic acid*, $C_{20}H_{30}O_2$, shining needles, m. p. 176—178°, has been isolated from the resin acids of the "black liquor" of the sulphate cellulose factories. When dissolved in a mixture of chloroform and acetic anhydride, the acid yields, on addition of a little concentrated sulphuric acid, a purplish-red coloration which passes through violet and blue into black. With hydrochloric acid and ferric chloride, the coloration is violet-blue. The residue obtained after evaporation with nitric acid becomes orange-yellow on addition of ammonia, instead of violet as with abietic acid. The specific rotation depends greatly on the solvent, the acid being dextrorotatory when dissolved in aromatic hydrocarbons, but lævorotatory in solution in aliphatic hydrocarbons. H. W.

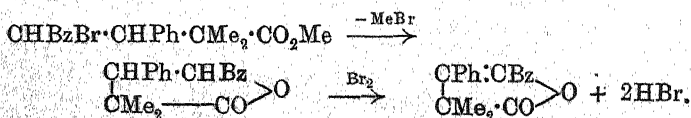
Catalytic Racemisation of Ethyl *l*-Mandelate. ALEX. MCKENZIE and HENRY WREN (*T.*, 1919, 115, 602—613).

The Bromination and Bromine Derivatives of Certain δ -Ketonic Esters. E. P. KOHLER and H. GILMAN (*J. Amer. Chem. Soc.*, 1919, 41, 683—692).—The course of the bromination of methyl γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate,



is found to depend on the temperature, the solvent, and the rate at which the bromine is added, the bromo-ester, saturated γ -lactones, and an unsaturated γ -lactone being formed.

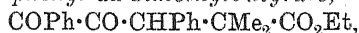
γ -Benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyric acid is obtained by boiling together benzene, phenyl styryl ketone, and ethyl α -bromo-*iso*-butyrate with some zinc suspended in the liquid in a copper cage, and hydrolysing the product by methyl-alcoholic-aqueous sodium hydroxide. It has m. p. 159°, and forms an *oxime*, m. p. 184.5°. The methyl ester, m. p. 92°, b. p. 200°/25 mm., is formed in the usual way from the acid (compare A., 1911, i, 863). When the ester, dissolved in chloroform, is slowly treated with bromine in the cold, the chief product is methyl γ -bromo- γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate, m. p. 125° (*ibid.*, 864). If the temperature is raised or the chloroform is removed by distillation instead of evaporation in a current of dry air, methyl bromide is lost, and two stereoisomeric, saturated γ -lactones are formed (*ibid.*), whilst a crotonolactone is produced if the reaction is carried out in methyl alcohol or the bromine is added rapidly, thus:



The original acid is easily converted into the δ -lactone (*ibid.*,

863), $\text{CHPh} \begin{smallmatrix} \text{CH-CPH} \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix} \text{O}$, by dissolving it in acetic anhydride containing a few drops of concentrated sulphuric acid. This lactone reacts with bromine in carbon tetrachloride to form an unstable dibromide which decomposes into the above bromo-ester and a saturated γ -lactone in methyl alcohol, but if bromination is carried out in methyl alcohol, an isomeric *bromo-ester*, m. p. 172° , is formed. The two esters both yield the γ -lactone, m. p. 115° , when left with methyl-alcoholic hydrogen bromide, but they behave differently on heating. The one with m. p. 125° decomposes at about 130° into the unbrominated ester, m. p. 92° , the corresponding acid, the γ -lactone, m. p. 115° , and the crotonolactone. The isomeride, m. p. 172° , decomposes at about 180° into benzoyl bromide, a small amount of the crotonolactone, and much uncrystallisable oil.

The above γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylcrotonolactone is obtained in pale yellow needles, m. p. 117° , by heating the original acid with bromine in carbon tetrachloride solution. The reaction proceeds briskly at first, but the final stage requires several hours, and it obviously follows a similar course to the bromination of the ester (above). The lactone may be reduced to the original acid by means of zinc and acetic acid. It gives a deep yellow solution in alcoholic potassium hydroxide, which deposits a yellow solid on acidifying, and this soon fades and produces the lactone again. With alcoholic hydrogen chloride, the lactone forms *ethyl γ -keto- γ -benzoyl- β -phenyl- $\alpha\alpha$ -dimethylbutyrate*,



which crystallises in yellow needles, m. p. 93° , and may be hydrolysed to the free *acid*, m. p. 145° . The *dioxime* of this, m. p. 186° , is formed when the lactone is boiled with hydroxylamine hydrochloride and barium carbonate in alcohol. J. C. W.

Statics and Dynamics of the two Phthalyl Chlorides. WILHELM CSÁNYI (*Monatsh.*, 1919, 40, 81—92).—Phthalyl chloride exists in two tautomeric modifications, a solid and a liquid. The equilibrium in the melt is toward the side of the lower melting modification, and can only be reached from this side. The solid modification is the stable one. The equilibrium is independent of the temperature, hence the heat change accompanying the change from one modification to the other must be very small or zero. The equilibrium is set up extremely slowly at low temperatures, but with increase in temperature the velocity of the change to the stable form increases rapidly, so that at the boiling point it is almost instantaneous. The mean temperature-coefficient of the transition velocity is 1.6 for 10° . The velocity of the change was determined at 130° , the amount changed at measured intervals being deduced from the melting point of the mixture. It is shown that the reaction is unimolecular, and the velocity constant has the value 0.036 . The natural melting point of the system is

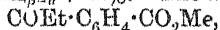
practically identical with the melting point of the lower melting modification. An eutectic is formed at 8° , and consists of 23 parts of the higher melting variety to 77 parts of the lower melting variety.

J. F. S.

Constitution of Aliphatic γ -Ketonic Acids and the Aromatic *o*-Aldehydo- and *o*-Ketonic-carboxylic Acids and their Derivatives. KARL VON AUWERS and ANNA HEINZE (*Ber.*, 1919, 52, [B], 584—601).—Some new examples of the application of optical measurements to the determination of chemical constitution.

Lævulic acid, b. p. $153^\circ/14$ mm., gives the following values: $E\Sigma_a - 0.03$, $E\Sigma_D - 0.01$, $E\Sigma_{\beta-a} + 2\%$, $E\Sigma_{\gamma-a} + 1\%$, calculated for the usual formula $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$. Its acetyl derivative, m. p. 78° , gives values which agree with the isomeric γ -lactone structure, $E\Sigma_a + 0.15$, $E\Sigma_D + 0.16$, $E\Sigma_{\beta-a} + 4\%$, $E\Sigma_{\gamma-a} \pm 0\%$, that is, it is really γ -acetoxyvalerolactone, $\text{OAc} \cdot \text{CMe} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$.

The phthalides show considerable exaltations, thus: phthalide itself, m. p. 73° , $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 27\%$; *o*-chlorophthalide, from *o*-phthalaldehydic acid and thionyl chloride, m. p. 61° , $E\Sigma_a + 0.57$, $E\Sigma_D + 0.58$; diethylphthalide, m. p. 54° , b. p. $158^\circ/17$ mm. (Bauer, A., 1904, i, 417), $E\Sigma_a + 0.51$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$. The optical properties of the ψ -esters of *o*-aldehydo- or *o*-keto-acids agree with those of the phthalides, whilst the normal esters compare with the parent aldehyde or ketones. The ψ -esters are, therefore, phthalides, as Egerer and Meyer assumed (A., 1913, i, 269). Methyl *o*-aldehydo-benzoate, m. p. 97° , has $E\Sigma_a + 0.75$, $E\Sigma_D + 0.77$, $E\Sigma_{\beta-a} + 37\%$, $E\Sigma_{\gamma-a} + 41\%$ (benzaldehyde: $+0.99$, $+1.02$, $+45\%$, $+49\%$), and the ψ -ester, α -methoxyphthalide, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{CH} \cdot \text{OMe}$, m. p. $46\text{--}47^\circ$, b. p. $145.5\text{--}146^\circ/12$ mm., compares with the above phthalides; $E\Sigma_a + 0.48$, $E\Sigma_D + 0.48$, $E\Sigma_{\beta-a} + 22\%$, $E\Sigma_{\gamma-a} + 22\%$. *o*-Propionylbenzoic acid, m. p. 93° , gives values which suggest that in the molten state the acid contains some of the isomeric hydroxyethylphthalide; $E\Sigma_a + 0.52$, $E\Sigma_D + 0.53$, $E\Sigma_{\beta-a} + 22\%$. The methyl ester,



from the silver salt and methyl iodide, b. p. $157\text{--}158^\circ/19$ mm., gives the values $E\Sigma_a + 0.53$, $E\Sigma_D + 0.55$, $E\Sigma_{\beta-a} + 26\%$, $E\Sigma_{\gamma-a} + 29\%$, which compare with those of propiophenone, $+0.43$, $+0.48$, $+29\%$, $+31\%$, whereas the ψ -ester, prepared by the action of the alcohol and sulphuric acid, is really α -methoxy-*o*-ethylphthalide, b. p. $157^\circ/17$ mm., $E\Sigma_a + 0.53$, $E\Sigma_D + 0.56$, $E\Sigma_{\beta-a} + 25\%$, $E\Sigma_{\gamma-a} + 26\%$. Methyl *o*-benzoylbenzoate, m. p. 52° , $E\Sigma_a + 0.90$, $E\Sigma_D + 0.95$, $E\Sigma_{\beta-a} + 40\%$, $E\Sigma_{\gamma-a} + 45\%$, and the ethyl ester, m. p. 58° , $E\Sigma_a + 1.00$, $E\Sigma_D + 1.06$, $E\Sigma_{\beta-a} + 39\%$, compare with benzophenone, $E\Sigma_a + 0.98$, $E\Sigma_D + 1.09$, $E\Sigma_{\beta-a} + 44\%$, whilst the ψ -ester, m. p. 56° , $E\Sigma_a + 0.52$, $E\Sigma_D + 0.57$, $E\Sigma_{\beta-a} + 23\%$, $E\Sigma_{\gamma-a} + 23\%$, is really α -ethoxy-*o*-phenylphthalide.

Ethyl hydrogen fumarate, m. p. 70° , $E\Sigma_a + 1.04$, $E\Sigma_D + 1.03$, $E\Sigma_{\beta-a} + 34\%$, shows greater exaltations than the normal ester, $E\Sigma_a + 0.64$, $E\Sigma_D + 0.67$, $E\Sigma_{\beta-a} + 25\%$, whereas the reverse is the case

with the phthalates; ethylhydrogen phthalate, $E\Sigma_a + 0.42$, $E\Sigma_D + 0.41$, $E\Sigma_{\beta-a} + 22\%$, ethyl phthalate, $E\Sigma_a + 0.56$, $E\Sigma_D + 0.58$, $E\Sigma_{\beta-a} + 22\%$. Methyl phthalate, whether prepared from the silver salt and methyl iodide, from the chloride and sodium methoxide or from the anhydride, alcohol, and hydrogen chloride, has the values $E\Sigma_a + 0.56$, $E\Sigma_D + 0.57$, $E\Sigma_{\beta-a} + 24\%$, $E\Sigma_{\gamma-a} + 27\%$.

Comparing ψ -esters with the normal esters, it appears that their boiling points are very close together, but that ψ -esters have the higher densities and lower refractive indices. For the details of densities and refractive indices, the original should be consulted.

J. C. W.

The Constitution of the Truxillic Acids and of Truxone.

HANS STOBBE (*Ber.*, 1919, **52**, [B], 1021—1028).—The formulæ

$\text{Ph}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$
 $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{CHPh}$ and $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ have been assigned to

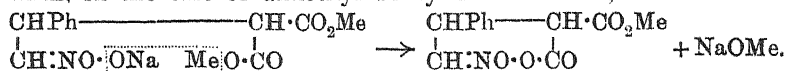
α - and β -truxillic acids. Whilst, however, the latter may be regarded as well established, the former is not so definitely proved, and depends chiefly on the determination of the molecular weight of the amyl ester, the failure to obtain benzil by oxidation, the formation of an abnormal polymeric anhydride which does not give a fluorescein, and the conversion into truxone. The molecular weight of the latter has not been directly determined, and its formulation is deduced from its relationship to truxene, truxenequinone, and dihydrotruxone. Truxenequinone has, however, been shown to be identical with tribenzoylenebenzene, $\text{C}_{27}\text{H}_{12}\text{O}_3$, and since it is readily formed by the oxidation of truxene, it seems very probable that the latter is tribenzoylenebenzene, $\text{C}_{27}\text{H}_{18}$, and that truxone has therefore the molecular formula $\text{C}_{27}\text{H}_{18}\text{O}_3$. Its formation from a number of substances, however, shows that the molecule of α -truxillic acid cannot contain more than eighteen carbon atoms, and this is supported by evidence from the molecular weights of ethyl dibromo- α -truxillate and ethyl hexachloro- α -truxillate.

To obtain further insight into the depolymerisation of the truxillic acids, the author has reinvestigated their action towards sulphuric acid; it is found that only the α -acid undergoes depolymerisation with formation of truxone, and that the latter is not directly produced from α -truxillic acid, but is formed by the action of the sulphuric acid on the *trans*- or *cis*-cinnamic acid, which is the primary product of the change. The only positive evidence in favour of the usual formula for α -truxillic acid is thereby greatly discounted, and it appears possible to the author that the α - and β -acids are structurally identical, and therefore stereoisomerides, the difference in their behaviour being due to the relative positions of the phenyl and carboxyl groups with respect to the plane of the 4-carbon ring. Support for this hypothesis is deduced from a study of the absorption curves of α - and β -truxillic acids, which are found to be even more closely similar than those of the stereoisomeric cinnamic acids.

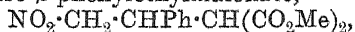
H. W.

The Addition of Nitromethane to Unsaturated Esters.

E. P. KOHLER and H. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, **41**, 764—770).—The experiments on the interaction of alcoholic sodionitromethane and unsaturated ketones (A., 1916, i, 404) have now been extended to $\alpha\beta$ -unsaturated esters. Deep orange or red solutions are obtained which, on acidification, yield red oils which do not crystallise and cannot be purified by distillation in a vacuum. Similar results are obtained when the condensation takes place in presence of small amounts of feebly basic reagents, such as sodamide, piperidine, potassium acetate, etc. These red oils are insoluble in sodium carbonate, and their colour is not affected on acidification. They may be heterocyclic compounds formed by elimination of sodium methoxide from the metallic derivatives. Thus, in the case of dimethyl benzylidenemalonate,



It was finally shown that, in order to isolate the additive product of nitromethane and to avoid the formation of these red oils, the experiments should be made in dry methyl-alcoholic solution in presence of sodium methoxide, the mixture immediately neutralised with a little glacial acetic acid, and saturated with hydrogen chloride. Under these conditions, dimethyl benzylidenemalonate gives methyl γ -nitro- β -phenylethylmalonate,

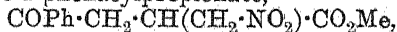


stout prisms, m. p. 63° , which is identical with the additive product of methyl sodiomalonate and β -nitrostyrene; this is an example of a new type of reaction, which is being further investigated. With alkalis, this substance is decomposed, whilst boiling hydrochloric acid yields phenylsuccinic acid. Bromine in carbon tetrachloride gives a monobromo-derivative, m. p. 158° .

The additive product of nitromethane and dimethyl cinnamylidenemalonate, $\text{CHPh} \cdot \text{CH} \cdot \text{CH}(\text{CH}_2 \cdot \text{NO}_2) \cdot \text{CH}(\text{CO}_2\text{Me})_2$, can also be obtained in benzene solution with a yield of 65%. In methyl alcohol, the yield is 87%. The nitro-ester crystallises in square plates, m. p. $74\text{--}75^\circ$.

The authors have prepared esters of benzoylacrylic acid by brominating esters of benzoylpropionic acid, and subsequently eliminating hydrogen bromide. Methyl benzoylacrylate was obtained in 92% yield as a yellow oil, b. p. 191° at 40 mm., and solidifying at 32° .

Methyl β -nitro- α -phenacylpropionate,



melts at 57° .

Two formulæ are possible for a substance of this type, because the ethylenic linking in the ester of benzoylacrylic acid is conjugated both with the carbonyl and with the carboxyl group. The foregoing constitution assigned to it is supported by the fact that when sodiomalonic esters combine with methyl benzoylacrylate, the sodium atom becomes attached to the carbon atom furthest from the carboxyalkyl group.

With boiling hydrochloric acid it yields benzoylpropionic acid. Bromine in chloroform gives rise to two isomeric monobromo-derivatives, separable owing to their differing solubility in cold methyl alcohol. The sparingly soluble one crystallises in plates, m. p. 125°. The other forms needles, m. p. 59°. F. C.

Bile Acids. V. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1919, 104, 284—292. Compare A., 1914, i, 487).—The *isodioxime* of bilianic acid when heated with 20% hydrochloric acid yields a substance, isolated by means of its copper salt, which crystallises in white needles decomposing at 228—230°. It is believed that this product is *aminocarboxybilianic acid isooxime*, $C_{24}H_{38}O_9N_2$, formed by the opening of only one of the two lactam rings present in bilianic acid. Such an acid should contain four carboxyl groups, three of which were present in bilianic acid, but only three were titratable by direct means. It is considered that the fourth is protected by the adjacent amino-group, since an increased titration value was obtained after treatment with formaldehyde by the technique of Sørensen. Cholic acid oxime, $C_{24}H_{37}O_7N$, begins to decompose at 160°. The oxime treated with strong sulphuric acid on the water-bath gave the *isooxime*, $C_{24}H_{37}O_7N$, long, hexagonal needles, decomp. 273—275°. By the action of hydrochloric acid on the *isooxime*, a substance, $C_{24}H_{39}O_8N$, was obtained in rhombohedra, m. p. 194—195°. This is apparently *aminocarboxycholeic acid*. After melting, it sets again, and finally decomposes at 274—275°, the decomposition point of the *isooxime*. These experiments support the work of Borsche and Rosenkranz (this vol., i, 276) on the structural relationship between bilianic acid and cholic acid. J. C. D.

Attempted Synthesis of Fisetol. ADOLF SONN (*Ber.*, 1919, 52, [B], 923—928).—The synthesis of fisetol (ω -hydroxyresacetophenone) has been attempted by several methods, which, however, have not been completely successful (compare Tambor and Du Bois, A., 1918, i, 395).

Chloroacetonitrile and resorcinol monomethyl ether react in ethereal solution under the influence of zinc chloride and dry hydrogen chloride to yield the 2-methyl and 4-methyl ether of ω -chlororesacetophenone, which are separated by taking advantage of the volatility of the latter with steam; the former has m. p. 173—174° (uncorr.). Similarly, bromoacetonitrile and resorcinol dimethyl ether yield ω -bromoacetoresorcinol dimethyl ether, m. p. 102—104° after previous softening, which is probably converted by potassium acetate into the corresponding acetate, prisms, m. p. 75°. Resorcinol and bromoacetonitrile yield a *product*, m. p. 127° after softening, but, as in the case of the dimethyl ether, the analytical results point to a partial displacement of bromine during the condensation. ω -Phenoxyresacetophenone,
 $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot OPh$,
 forms coarse, shining plates, has m. p. 204—205° after softening at

200° (attempts to remove the phenyl group were unsuccessful); its *dimethyl ether* forms thin prisms or needles, m. p. 115° after previous softening. *ω-Ethoxyresacetophenone* has m. p. 136—137° after softening; its *diethyl ether*, coarse prisms, and *dimethyl ether*, irregular plates, have m. p.'s 66° and 56—57° respectively.

H. W.

The Preparation of β -Aminopropiophenone. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 841—847).—Amino-derivatives of ketones cannot be satisfactorily prepared by the action of ammonia on the corresponding halogen derivatives owing to the further substitution of the hydrogen of the ammonia. Amides of ketonic acids behave abnormally in the Hofmann reaction, and give rise to internal condensation products (compare Biedermann, A., 1892, 471).

Gabriel prepared β -aminopropiophenone from *p*-bromopropylphthalimide. This was converted into the corresponding alcohol, acid, and acid chloride, which by the Friedel and Craft reaction and subsequent hydrolysis yielded the desired product (A., 1908, i, 181).

The author has prepared β -phthaliminopropionic acid from the *isoamyl ester* of β -chloro- or iodo-propionic acid. The yield, however, was only 40%. In order to avoid the formation of substituted phthalamic acids, the hydrolysis is effected with 40% hydrobromic acid instead of sodium hydroxide. The method finally adopted is indicated by the scheme β -iodopropionic acid \rightarrow β -iodopropionyl chloride \rightarrow β -iodopropiophenone \rightarrow β -phthaliminopropiophenone \rightarrow β -aminopropiophenone. The yields in the last stages are 90%, 68%, and 95%.

The β -chloro-derivative of propionic acid may also be used, but its preparation is less easy than that of the iodo-derivative. *isoAmyl β -chloropropionate* is miscible with most organic solvents except light petroleum, and boils at 207—208°/740 mm. The corresponding *iodo*-compound has b. p. 183°/140 mm. (slight decomp.). *isoAmyl β -phthaliminopropionate*, m. p. 61°, was obtained in a 70% yield from either of the two foregoing compounds.

β -Chloropropiophenone decomposes on distillation in a vacuum into hydrogen chloride and phenyl vinyl ketone.

β -Iodopropiophenone, m. p. 61°, is insoluble in water and crystallises from alcohol. The acid chloride of β -iodopropionic acid is exceedingly irritating to the eyes, and readily decomposes on distillation.

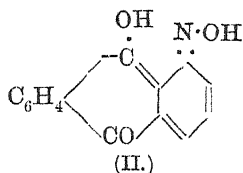
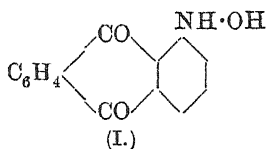
F. C.

A New Synthesis of Styryl Methyl Ketone. G. LANGLOIS (*Compt. rend.*, 1919, **168**, 1052—1054).—Acetyl chloride reacts with styrene in the presence of stannic chloride to give β -chloro- β -phenylethyl methyl ketone, which, on the addition of diethyl aniline, loses the elements of hydrogen chloride, giving styryl methyl ketone.

W. G.

Constitution of Hydroxy- and Hydroxylamino-anthraquinone Salts. R. SCHOLL (*Ber.*, 1919, **52**, [B], 565—567).—In part, a denial of Baudisch's claim to priority (this vol., i, 211).

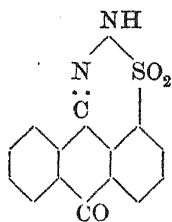
When a solution of 1-hydroxylaminoanthraquinone in alcohol is mixed with about two equivalents of sodium ethoxide and left in an atmosphere of nitrogen, a green *mono-sodium* salt is deposited. This shows that the compound behaves as a benzenoid structure (I) rather than in the isomeric form (II), which would give a disodium salt.



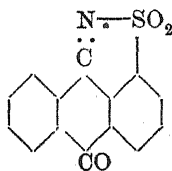
J. C. W.

Cyclic Compounds from Anthraquinone-1-sulphonic Acid.

FRITZ ULLMANN and PAUL KERTÉSZ (*Ber.*, 1919, **52**, [B], 545—558).—Anthraquinone is sulphonated in the presence of mercury, and the potassium anthraquinone-1-sulphonate (Iljinsky, *A.*, 1904, i, 176; Schmidt, *ibid.*, 256) is heated with a mixture of phosphorus pentachloride and oxychloride at 120°. *Anthraquinone-1-sulphonyl chloride* (compare MacHoul, *Diss.*, Freiburg, 1880) crystallises from nitrobenzene or toluene in golden-yellow prisms, m. p. 218° (corr.), changes into 1-chloroanthraquinone when kept at 220°, and is hydrolysed by boiling water to *anthraquinone-1-sulphonic acid*. This forms colourless leaflets, m. p. 214° (corr.), and yields a *barium* salt, insoluble, white needles, a *calcium* salt, soluble in boiling water, a golden-yellow *lead* salt, crystallising from boiling water, a *hydrazine* salt, $N_2H_4(C_{14}H_8O_5S)_2$, and an *aniline* salt, pale yellow needles, m. p. 291°. (The *aniline* salt of anthraquinone-2-sulphonic acid is silvery-white and has m. p. 314°.)



The reactions of the sulphonyl chloride with various bases are described. Hydrazine hydrate reacts at 30° to give the *anhydride of anthraquinone-1-sulphonhydrazide* (annexed formula), which crystallises from aniline or nitrobenzene as a yellow powder, and yields a *sodium* salt, yellow leaflets, a *silver* salt, pale yellow leaflets, a *methyl* derivative (with methyl sulphate), silvery leaflets, decomp. 239°, and an *acetyl* derivative, pale yellow needles, m. p. 237° (decomp.). Ammonia gives the *anhydride of 1-anthraquinonesulphonamide* (annexed formula), which crystallises from pyridine or nitrobenzene in pale yellow, felted needles, m. p. 321° (corr.). Aniline gives *anthraquinone-1-sulphonanilide*, golden-yellow needles from toluene, m. p. 216° (corr.), and methylaniline yields *anthraquinone-1-sulphonmethylanilide*, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot SO_2 \cdot NMePh$, pale yellow leaflets, m. p. 205°.



On nitration, the potassium salt of anthraquinone-1-sulphonic acid gives a mixture of 5- and 8-nitroanthraquinone-1-sulphonic acids. The former separates directly from the hot nitrating mixture, whilst the latter crystallises slowly when the filtrate is kept (compare Schmidt, *loc. cit.*). 5-Nitroanthraquinone-1-sulphonic acid forms a golden-yellow *potassium* salt, a white *barium* salt, and a *sulphonyl chloride*, yellow needles, m. p. 277° (corr.), which reacts with ammonia to give the *anhydride* of 5-nitroanthraquinone-1-sulphonamide, this crystallising from nitrobenzene in pale brown needles, m. p. 425° , and yielding the corresponding 5-amino-compound, dark violet leaflets, on reduction with alkaline hypsulphite. 8-Nitroanthraquinone-1-sulphonic acid forms a *potassium* salt, twice as soluble as the isomeride, and a *sulphonyl chloride*, yellow needles, m. p. 245° , which yields the *anhydride* of 8-nitroanthraquinone-1-sulphonamide, m. p. 314° (corr.). The nitro-compounds may be reduced by means of potassium sulphide; *potassium* 5- and 8-aminoanthraquinone-1-sulphonates crystallise in violet needles, the 8-isomeride being the more soluble. The constitution and purity of the nitrated acids were elucidated by boiling them with hydrochloric acid and sodium chlorate, whereby they yielded 1-chloro-5-nitroanthraquinone, yellow, felted needles, m. p. 314° (corr.) (convertible into the known 1-nitro-5-aminoanthraquinone), and 1-chloro-8-nitroanthraquinone, m. p. 263° (corr.).
J. C. W.

Reduction Products of Hydroxymethylenecamphor. II. Mechanism of the Hydrogenation of Hydroxymethylenecamphor with Hydrogen and Nickel. HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, 2, 205—221. Compare this vol., i, 29).—The hydrogenation of hydroxymethylenecamphor in the presence of a specially prepared nickel catalyst can be made use of in a study of the kinetics of such reactions, and a series of experiments with this aim are now described. A graphic representation of the hydrogen absorbed from time to time shows that the curves are nearly hyperbolic when the abscissæ, x , are taken from the values, $\text{time} \times \text{weight of catalyst} / \text{initial weight of hydroxymethylenecamphor}$, and the ordinates, y , are the percentages of hydrogen absorbed, calculated on the theoretical requirement. These curves are treated mathematically, and, after making corrections for probable disturbing factors, such as secondary reactions caused by nickel compounds, it appears that the main reaction is a bimolecular one. That is, not only does the quantity of hydroxymethylenecamphor fall off, but the amount of hydrogen transferred as well, or, in other words, the catalyst continually decreases in activity. This explains why such a large quantity of nickel is required in this case to achieve a rapid and complete reduction.

In this reduction, as in so many similar cases, much more hydrogen is absorbed than is theoretically required, but, as a matter of fact, the reduction is actually complete when only about 80—90% of the required volume of gas has disappeared. This is

not due to experimental errors, but chiefly to the activation of the water by the nickel.

J. C. W.

Reduction Products of Hydroxymethylenecamphor. III. New Reactions of Methylenecamphor.

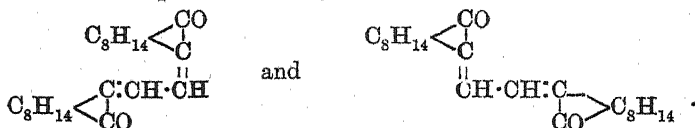
HANS RUPE and ARTHUR AKERMANN (*Helv. Chim. Acta*, 1919, 2, 221—233. Compare this vol., i, 29).—When camphylcarbinol is warmed with sodium in benzene solution, a new derivative, *s-dicamphylethane*,

$C_8H_{14} \begin{smallmatrix} CO \\ \diagup \diagdown \\ CH \cdot C_2H_4 \cdot CH \\ \diagdown \diagup \\ CO \end{smallmatrix} C_8H_{14}$, is produced. This crystallises in slender, white prisms, m. p. 209—211°, and its constitution is revealed by the fact that it may be obtained from camphylmethyl bromide by the Fittig and Wurtz method. It is assumed that water is eliminated from the carbinol, giving methylenecamphor and hydrogen (from the sodium), and that either two molecules of this compound condense and then combine with hydrogen, or one molecule is reduced to methylcamphor, which condenses with the methylenecamphor. The compound can also be obtained by boiling solutions of methylenecamphor in benzene or toluene with sodium, and then treating the product with water. In this case, the necessary hydrogen is supposed to be derived from an enolic form of the compound obtained by the union of two molecules of methylenecamphor. The fact that both series of reactions proceed better in moist benzene supports the given interpretations of the mechanism.

In the Fittig-Wurtz reactions, and in the above processes when moisture is excluded, small quantities of an *isomeride* are formed, which is slightly less soluble in light petroleum and crystallises in glistening, crossed prisms, m. p. 258—259°. Probably it has the

formula, $C_8H_{14} \begin{smallmatrix} CO \\ \diagup \diagdown \\ CMe \cdot CH_2 \cdot CH \\ \diagdown \diagup \\ CO \end{smallmatrix} C_8H_{14}$.

Chloromethylenecamphor (A., 1916, i, 409) also reacts readily with sodium in ethereal solution, giving the *cis*- and *trans*-modifications of *dicamphoethandiene*,



The *cis*-modification crystallises from light petroleum in orange-yellow tetrahedra, m. p. 238—239.5°, whereas the *trans*-isomeride is insoluble and separates best from glacial acetic acid in slender, greenish-yellow needles, m. p. 282—283°.

Camphylmethyl bromide does not react at all readily with magnesium, and its reaction with magnesium phenyl bromide is also not so vigorous as in the case of chloromethylenecamphor. The product, benzylcamphor, was also obtained with about the same optical properties by the reduction of benzylidenecamphor with sodium amalgam.

J. C. W.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. I. Position Isomerism and Optical Activity of Naphthyliminocamphors and Derivatives of Phenyliminocamphor. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (T., 1919, 115, 566—576).

Genetic Relationships of the Terpenes. OSSIAN ASCHAN (*Finska Kem. Jubilæumsnummer*, 1918, pp. 15; from *Chem. Zentr.*, 1919, i, 285).—A concise résumé of the chemistry of the terpenes.

H. W.

New Terpene in Finnish Turpentine. OSSIAN ASCHAN (*Technikern*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 284).—A new terpene hydrocarbon has been obtained by the fractional distillation of Finnish turpentine with steam; it has b. p. 163—165°, D_4^{20} 0.8628, $[\alpha]_D^{20} + 7.70^\circ$, and is a bicyclic, simply saturated terpene closely related to pinene. It yields pinene nitrosochloride with amyl nitrite and hydrochloric acid.

H. W.

Action of Finely Divided Metals on Pinene Vapour. PAUL SABATIER, ALPH. MAILHE, and G. GAUDION (*Compt. rend.*, 1919, 168, 926—930).—The metals used were copper, nickel, cobalt, and iron. When pinene vapour is passed over any of these metals at 350°, there is no evolution of gas, but a liquid is obtained which is less volatile than the original pinene and consists of terpenes isomeric with pinene and a small amount of polyterpenes. At higher temperatures there is an evolution of gas, the amount of which varies with the temperature and the nature of the metallic catalyst. With copper at 500° there is an abundant evolution of a gas, which is a mixture of hydrogen and olefines. With copper at 600—630° there is a still more marked evolution of gas, whilst the liquid product consists of a mixture of isoprene, olefines and diolefines, terpenes, and aromatic hydrocarbons, such as toluene, *m*-xylene, cymene, cumene, and methylethylbenzene. The yield of aromatic hydrocarbons was in one case 31% of the pinene used. With reduced nickel at 600°, a very energetic decomposition of the pinene occurs, a gas being evolved rich in hydrogen, carbon is deposited, and very little liquid product is obtained. With cobalt at 600°, the results obtained are intermediate between those obtained with nickel and copper, whilst reduced iron is similar to nickel in its effect.

W. G.

Finnish Turpentine. V. Formation of Terpin Hydrate and Terpeneol. OSSIAN ASCHAN (*Bidrag k  nn. Finlands natur och folk*, 1918, 77, pp. 30; from *Chem. Zentr.*, 1919, i, 284).—The author has endeavoured to find new methods of preparing terpin from pinene and dipentene. Preliminary experiments on the action of sulphuric acid of varying concentration on oil of turpentine without cooling showed that terpin (which is probably transiently formed under all conditions when pinene is converted

into dipentene by acids) was certainly produced at the ordinary temperature, but that at the high concentration, and possibly increased temperature, water was almost immediately eliminated and dipentene formed. It is important that stirring and cooling should be very efficient, thereby preventing decomposition of the terpin hydrate formed by the acid. With efficient stirring (ten hours) and using 45% sulphuric acid, 53.2% of the theoretical yield of terpin was obtained; during the greater part of the time, the temperature must be maintained at $+1^{\circ}$. *trans*-Terpin is formed as a by-product. Terpin is also produced by the action of sulphuric acid (45%) on nopinene (from American oil of turpentine).

Terpin may also be obtained by addition of water to dipentene (1 part) by treatment with sulphuric acid (55%; 6 parts) at -6° ; the crude product is remarkably pure, but may contain *trans*-terpin. The conversion of terpin hydrate by loss of water into terpineol is best effected by the action of oxalic acid solution (0.5%). The transformation of terpineol into pinene by means of formic acid is so successful that the process appears capable of technical application. An almost quantitative yield of terpin hydrate is obtained from terpineol (1 part) by the action of sulphuric acid (40%; 5 parts), the mixture being kept well stirred and cooled by ice.

Terpin hydrate can be prepared in good yield from the fraction of Finnish turpentine, b. p. $155-167^{\circ}$, which contains the terpenes related to pinene.

H. W.

Finnish Turpentine. VI. The Components of High Boiling Point. OSSIAN ASCHAN (*Bidrag känn. Finlands natur och folk*, 1918, 77, pp. 88; from *Chem. Zentr.*, 1919, i, 284—285).—A specimen of turpentine and a resin distillate obtained in the manipulation of the resin of *Pinus sylvestris* have been investigated, and terpene alcohol and cadinene have been obtained. The question whether cadinene exists as such in the fraction, b. p. $125-130^{\circ}/9$ mm., or whether its hydrochloride is formed by the action of hydrogen chloride on another sesquiterpene, remains undecided.

H. W.

Constituents of Higher Boiling Point in Finnish Turpentine. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, pp. 3; from *Chem. Zentr.*, 1919, i, 285).—Fractions b. p. $210-220^{\circ}$ and ca. 260° have been observed in Finnish turpentine in the products of the tar ovens and in those obtained by the distillation of resin with steam; they appear to consist of terpene alcohol and a sesquiterpene, and resemble that obtained from pine resin (preceding abstract). An unsaturated terpene alcohol, $C_{10}H_{17}OH$, has been isolated which is not identical with terpineol, but is possibly a mixture of the latter with other terpene alcohols. A sesquiterpene, $C_{15}H_{24}$, b. p. $260-263^{\circ}/760$ mm., D_4^{20} 0.9187, has also been obtained. It is unsaturated towards potassium permanganate, bromine, and hydrogen chloride, and is converted by the latter into cadinene dihydrochloride, m. p. $117-118^{\circ}$. Since cadinene, obtained from

this hydrochloride, has b. p. 271° , it cannot be identical with the original substance.

H. W.

The Sesquiterpene Fraction in the Volatile Portions of Pine Resin. OSSIAN ASCHAN (*Finska Kem. Medd.*, 1918, pp. 2; from *Chem. Zentr.*, 1919, i, 285).—A new terpene has been isolated from a distillate obtained during the manipulation of pine resin. Its *dihydrochloride*, $C_{15}H_{26}Cl_2$, forms shining, rhombic leaflets, m. p. $85-86^{\circ}$. It is possibly a bicyclic sesquiterpene, and may be related to cadinene.

H. W.

Some Constituents of French and American Rosins. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers*, 1919, 35, 148—154).—By repeated crystallisation from glacial acetic acid and alcohol, two pimaric acids, $C_{20}H_{30}O_2$, are isolated from French and American rosins, that from the former forming large, colourless crystals, m. p. 161° , $\alpha_D -80^{\circ}$, and that from the latter melting at the same temperature and having $\alpha_D +79^{\circ}$. The two acids differ in certain particulars, and are probably not optical isomerides. On heating in a vacuum or in a stream of carbon dioxide, both acids are converted into rosin-like anhydrides by the loss of a molecule of water from two of acid. The hydration of the anhydride of *l*-pimaric acid takes place slowly at the ordinary temperature by the action of water, and when it is crystallised from water-absorbing solvents, such as alcohol or acetic acid, inactive pimaric acid is obtained which, by ebullioscopic methods, gives figures indicating a double molecular weight. Resolution of the acid is effected by means of *d*-tetrahydroquinidine. By the action of bromine in carbon tetrachloride solution, both *d*- and *l*-pimaric acids give crystalline tribromo-substitution products, m. p. $115-118^{\circ}$, whilst with nitrous acid, greenish-blue, crystalline nitrosites, m. p. 99° , are obtained. When exposed to the air, *l*-pimaric acid slowly absorbs oxygen to the extent of two atomic proportions, and on distillation with aluminium, a hydrocarbon, $C_{19}H_{30}$, is produced, probably identical with or analogous to abietene or colophene. The rosins themselves probably consist mainly of anhydrides, hydration being a preliminary to the crystallisation of the rosin acids.

G. F. M.

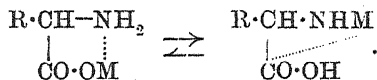
Synthetic Glucosides. III. A Contribution to the Constitution of Internally Complex Salts. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, 2, 242—265. Compare A., 1916, i, 832; 1917, i, 539).—I. *Constitution of Internally Complex Salts* [with L. WILBUSCHIEWICH].—It is now generally accepted that the metallic atom in internally complex salts of the α -amino- or α -hydroxy-acids is bound, not only to the carboxyl group, but to the α -substituent as well. That being so, it should be possible to obtain isomeric derivatives by the action of a suitable halogen compound on the salt, according to the scheme:



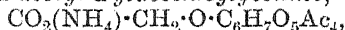
in which $\cdot\text{OH}$ might be written instead of $\cdot\text{NH}_2$. An indication that such a reaction might take place has already been given, namely, in the formation of tetra-acetylglucose salicylate and the tetra-acetylglucoside of salicylic acid by the action of acetobromoglucose on silver salicylate, and it is now shown that silver anthranilate reacts with ethyl iodide in warm toluene to form a mixture of *N*-ethylanthranilic acid and ethyl anthranilate.

In order to obtain pairs of isomerides at all, search must be made for a suitable halogen derivative. For example, silver salicylate and ethyl iodide only give ethyl salicylate. It is somewhat remarkable that acetobromoglucose is more suitable than any other derivative tested so far. This is of interest, because it opposes another interpretation of the reaction, which, without reference to internally complex salts, would suggest that any change at the α -amino- or α -hydroxyl group might be preceded by attachment of the haloid as such. Acetobromoglucose has practically no tendency to form quaternary salts with amines.

It is generally assumed that the metal is attached to the carboxylic residue by a main valency and to the amino- or hydroxyl group by residual affinity. The preponderance of ester in most of the above reactions is in keeping with this view, but it is possible to represent the salts as desmotropes, thus:



II. *Glucosides of α -Hydroxycarboxylic Acids.*—The silver salts of all the α -hydroxy-acids investigated so far react with acetobromoglucose to give isomerides, as in the case of salicylic acid. Ammonium β -tetra-acetyl-d-glucosidoglycollate,



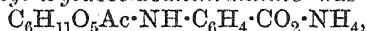
from silver glycollate, crystallises in concentric groups of felted needles, with about 2 mols. EtOH, which it loses at $95\text{--}100^\circ$, and has m. p. 157° , $[\alpha]_D^{18} - 35.6^\circ$. It yields β -d-glucosidoglycollic acid on hydrolysis with baryta or ammonia (Fischer and Helferich, A., 1911, i, 675).

Silver lactate gives tetra-acetyl-d-glucose dl-lactate, felted needles, m. p. 174° , $[\alpha]_D^{16} - 3.23^\circ$, and ammonium β -tetra-acetyl-d-glucosido-dl-lactate, m. p. 165° , $[\alpha]_D^{16} - 34.92^\circ$, which yields d-glucosido-dl-lactic acid, $[\alpha]_D^{17} - 36.58^\circ$, on hydrolysis.

The active and inactive mandelic acids give the following compounds: β -tetra-acetyl-d-glucosido-dl-mandelic acid, felted, white needles, m. p. $130\text{--}150^\circ$, $[\alpha]_D^{15}$ from -36.97° to -43.46° with different preparations, the corresponding derivative of d-mandelic acid, $\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4\cdot\text{O}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, highly refractive needles, m. p. 166° , $[\alpha]_D^{14} - 5^\circ$, and the derivative of l-mandelic acid, white needles, m. p. 132° , $[\alpha]_D^{15} - 82.4^\circ$; β -tetra-acetyl-d-glucose d-mandelate, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}_2\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, snow-white needles, m. p. 163° , $[\alpha]_D^{14} + 5.13^\circ$ (yield four times as great as that of the glucoside), and the l-mandelate, m. p. 134° , $[\alpha]_D^{12} - 63.09^\circ$, which is much more

soluble in alcohol than the isomeride, it being possible to separate the inactive *dl*-mandelate into the two esters by fractional crystallisation. The tetra-acetates may be hydrolysed by baryta or dilute ammonia solutions to the following: *d*-glucosido-*dl*-mandelic acid, $C_6H_{11}O_5 \cdot O \cdot CHPh \cdot CO_2H$, also designated *prulaurasinic acid*, because of its relationship to the cyanogenetic glucoside, prulaurasin, a white, hygroscopic powder, crystallising with $1EtOH$, $[\alpha]_D^{25} - 28.17 - 33.18^\circ$, which is hydrolysed by emulsin, but does not reduce Fehling's solution, and forms a very hygroscopic ammonium salt, $0.5H_2O$, $[\alpha]_D^{25} - 36.12^\circ$; and *d*-glucosido-*l*-mandelic acid, $[\alpha]_D^{25} - 138.6^\circ$, and *d*-glucosido-*d*-mandelic acid, $[\alpha]_D^{25} + 51.39^\circ$, also called *prunasinic acid* and *sambunigrinic acid* respectively.

III. *Glucosides of Anthranilic Acid*.—Silver anthranilate reacts with acetobromoglucose to form *tetra-acetylglucose anthranilate*, $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_7O_5Ac_4$, m. p. 177° , $[\alpha]_D^{25} - 58.12^\circ$, and *N-tetra-acetylglucosidoanthranilic acid*, $CO_2H \cdot C_6H_4 \cdot NH \cdot C_6H_7O_5Ac_4$, white needles, m. p. 181° , $[\alpha]_D^{25} - 63.89^\circ$. The latter is a representative of the somewhat obscure group of *N*-glucosides. It may be hydrolysed by methyl-alcoholic ammonia to the very hygroscopic ammonium *N*-*d*-glucosidoanthranilate, $[\alpha]_D^{25} - 85.66^\circ$, which reduces Fehling's solution, and may be converted into the *silver* salt, but the free acid is too unstable to be isolated. In one hydrolysis, ammonium *N*-acetyl-*d*-glucosidoanthranilate was formed,

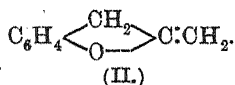
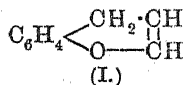


in stout, limpid crystals, m. p. $80 - 85^\circ$.

J. C. W.

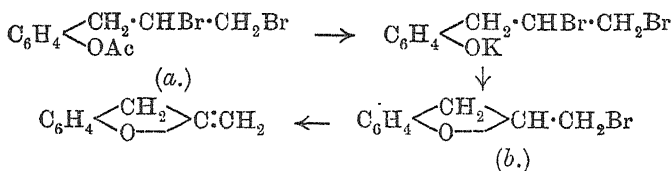
The Tannin of the Canadian Hemlock (*Tsuga Canadensis*, Carr.). RODGER JAMES MANNING and MAXIMILIAN NIERENSTEIN (T., 1919, 115, 662—673).

Cyclic Ethers from *o*-Allyl Phenols ; Methylenecoumarans [1-Methylene-1:2-dihydrobenzofurans]. ROGER ADAMS and R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, 41, 648—665).—The following series of reactions with *o*-allylphenol has been studied: (a) acetylation, (b) bromination, and (c) treatment of the dibromide with alcoholic potassium hydroxide. These are the reactions involved in the production of flavones by Kostanecki's method from *o*-acetoxyphenyl styryl ketones, and it was expected that in this case the parent of the flavones, namely, "chromene" (I), would be formed. Instead, the last operation takes a different course, and the product is 1-methylenecoumaran (II).



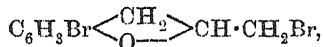
The formation of the methylenecoumaran appears to be a general reaction, and the mechanism of the process was proved as follows. When the *o*-acetoxy- β -dibromopropylbenzene is treated with one molecular proportion of sodium ethoxide, the acetyl group is eliminated and a monobromo-cyclic ether formed, which yields the known 1-methylcoumaran on reduction with zinc and hydrochloric

acid, and 1-methylenecoumaran when boiled with alcoholic potassium hydroxide. The reactions can only be interpreted as follows:



o-Acetoxyallylbenzene, from *o*-allylphenol and acetic anhydride, has b. p. 123—124°/20 mm., D^{24}_D 1.031, n^{20}_D 1.508, and its *dibromide* (a) forms white crystals, m. p. 42°; 1-bromomethylcoumaran (b) has b. p. 144—145°/20 mm., D^{25}_D 1.453, n^{20}_D 1.575; and 1-methylenecoumaran is a pleasant-smelling oil, b. p. 93—94°/20 mm., 196—197°/744 mm., D^{24}_D 1.050, n^{20}_D 1.555, which reacts with bromine in carbon disulphide at 0° to form 1-bromomethylenecoumaran, $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \\ \text{O} \end{array} \text{C} \cdot \text{CHBr}$, b. p. 134—138°/25 mm., D^{23}_D 1.472, n^{20}_D 1.584.

In the case of *o*-allylphenol, it is necessary to acetylate before the bromination, because the free phenol reacts in a complicated manner with bromine. When slowly treated with bromine in carbon disulphide at 0° or below, and the product is slowly distilled in a partial vacuum, three main fractions are obtained. Fraction I, b. p. 90—125°/20 mm., is the greatest, and consists chiefly of 1-methylcoumaran, b. p. 93—94°/23 mm., D^{24}_D 1.032, n^{20}_D 1.531 (Claisen, A., 1913, i, 1176; 1915, i, 707). Fraction II, b. p. 125—146°/20 mm., contains two isomerides with b. p. 142°/20 mm.; one is 4-bromo-1-methylcoumaran, D^{24}_D 1.414, n^{20}_D 1.569, and the other is 1-bromomethylcoumaran, since it yields 1-methylenecoumaran when the mixture is boiled with alcoholic potassium hydroxide, and 1-methylcoumaran when boiled with zinc and hydrochloric acid. Fraction III, b. p. 180—210°/20 mm., contains chiefly α -4-dibromo-1-methylcoumaran,



b. p. 189—194°/20 mm., D^{24}_D 1.795, n^{20}_D 1.607, for, when reduced by zinc and hydrochloric acid, it yields the above 4-bromo-1-methylcoumaran, and when treated with alcoholic potassium hydroxide it forms 4-bromo-1-methylenecoumaran, b. p. 148°/30 mm., D^{24}_D 1.483, n^{20}_D 1.595.

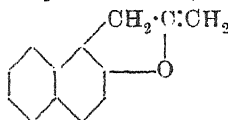
An attempt was made to obtain *o*- $\beta\gamma$ -dibromopropylphenol from its methyl ether. *o*-Allylanisole, b. p. 101—102°/22 mm., D^{24}_D 0.972, n^{20}_D 1.526, prepared by the action of methyl sulphate on *o*-allylphenol, reacts with bromine in carbon disulphide, however, to form some of the same compounds as the free phenol.

4-Bromo-2-allylphenol (Claisen, *loc. cit.*) yields the above 4-bromo-1-methylcoumaran when heated with pyridine hydro-

chloride, and this may also be obtained by brominating 1-methylcoumaran. 4-Bromo-2-allylphenyl benzoate has b. p. 234—236°/25 mm., D^{24}_D 1.308, n^{25}_D 1.589, and its dibromide, m. p. 98.5°, yields the above 4-bromo-1-methylenecoumaran when boiled with alcoholic potassium hydroxide.

3-Allyl-*p*-cresol and 3-allyl-*o*-cresol (*ibid.*) give the following compounds: 3-allyl-*p*-tolyl acetate, b. p. 139°/22 mm., D^{20}_D 1.022, n^{20}_D 1.507, its dibromide, long, white needles, m. p. 77.5°, and 4-methyl-1-methylenecoumaran, b. p. 113°/17 mm., D^{20}_D 1.043, n^{20}_D 1.556; and 3-allyl-*o*-tolyl acetate, b. p. 128°/14 mm., D^{20}_D 1.023, n^{20}_D 1.507, its dibromide, b. p. 210°/20 mm., and 6-methyl-1-methylenecoumaran, b. p. 101—102°/15 mm., D^{20}_D 1.043, n^{20}_D 1.553.

1-Allyl- β -naphthol (Claisen, A., 1912, i, 965) forms an acetate, b. p. 186—189°/17 mm., D^{25}_D 1.111, n^{25}_D 1.584, the dibromide of which, fibres, m. p. 89°, yields 2-methylene-2 : 3-dihydro-4 : 5- $\alpha\beta$ -naphthafuran (annexed formula), m. p. 55°, b. p. 188—190°/17 mm., when boiled with sodium ethoxide solution.



3-Allylsalicylic acid and its methyl ester (Claisen, *loc. cit.*) cannot be acetylated, but this is no hindrance to the above reaction, as the hydroxyl group needs no protection during bromination. Methyl 3- β -dibromopropylsalicylate, m. p. 72—72.5°, and the free acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, needles, m. p. 162.5—163.5°, both yield 1-methylenecoumaran-6-carboxylic acid, m. p. 152°, when boiled with alcoholic potassium hydroxide, and this compound gives 1-bromomethylenecoumaran-6-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3\langle\frac{\text{CH}_2}{\text{O}}\rangle\text{C}\cdot\text{CHBr}$, m. p. 222—223°, when treated with bromine in carbon disulphide at 0°. J. C. W.

Syntheses of Chromans and Coumarans. R. E. RINDFUSZ (*J. Amer. Chem. Soc.*, 1919, **41**, 665—670).—Three simple methods for the preparation of chroman and coumaran have been discovered. I. Phenyl γ -hydroxypropyl ether, from trimethylenechlorohydrin and sodium phenoxide, is heated with zinc chloride, giving chroman in 30—35% yield, or phenyl β -hydroxyethyl ether, from ethylene chlorohydrin and sodium phenoxide, is similarly treated, giving a 25% yield of coumaran. II. Phenyl γ -bromopropyl ether or phenyl β -bromoethyl ether, from sodium phenoxide and the dibromides, heated with zinc chloride, gives a 65% yield of chroman or a 30—40% yield of coumaran as the case may be. III. Mixtures of phenol and the chlorohydrins are heated with zinc chloride, but the yields are not so good.

It is obvious that substituted chromans and coumarans could be made very readily from substituted phenols. J. C. W.

Cinchona Alkaloids. II. 5-Azo- and 5-Amino-compounds of Cupreine, Hydrocupreine, and their Methyl and Ethyl Ethers. G. GIEMSA and J. HALBERKANN (*Ber.*, 1919, **52**, [B], 906—923. Compare this vol., i, 33).—5-Benzeneazocupreine, anhy-

drous, microscopic needles, m. p. 129—130°, is obtained by the action of diazotised aniline on an alkaline solution of cupreine; the corresponding *sodium p-sulphonate* (from diazotised sulphanilic acid) forms ruby-red crystals ($+6\text{H}_2\text{O}$), which have m. p. 212° (decomp.) after darkening at 200°, whilst the free *p-sulphonic acid* separates from water in red, prismatic needles ($+3\text{H}_2\text{O}$), which, when dehydrated, decompose at 257° after darkening at 250°. Reduction of the azo-compounds, preferably with sodium hyposulphite in alkaline solution, leads to the formation of *5-aminocupreine*, an unstable, non-crystalline mass, m. p. generally between 170° and 195°, $[\alpha]_D^{20} - 121.2^\circ$ (in ether), $[\alpha]_D^{20} - 18.4^\circ$ (in alcohol). The salts are stable; the *platinichloride*, microcrystalline needles, decomposing at about 220°; the *monosulphate*, yellow, prismatic needles, which are completely decomposed at 232°; the *disulphate*, red prisms, which darken at about 170° and decompose above 200° (this is the most stable sulphate and separates from solutions containing more than the requisite quantity of sulphuric acid); the *trioxalate*, dull red powder, m. p. 152—153° (decomp.); and the *tetrasulphate*, colourless, microscopic needles, m. p. 187° (decomp.), after previous sintering and darkening, are described. *5-Benzoylaminocupreine* forms a grey powder, m. p. about 135°, after previous contraction. $[\alpha]_D^{20} + 39.8^\circ$ (in alcohol); *5-dibenzoylaminocupreine* resembles the monobenzoyl derivative, melts indefinitely at 165°, and has $[\alpha]_D^{20} + 41.6^\circ$ (in alcohol); *tribenzoylaminocupreine* crystallises in colourless, rhombic plates, m. p. 183°, $[\alpha]_D^{20} + 131.1^\circ$ (in alcohol). The primary product of the interaction of 5-aminocupreine and phenylthiocarbimide in alcoholic solution appears to be the *thiocarbamide*, small, colourless needles or plates, m. p. 247° (decomp.), after much previous softening, which, however, readily loses hydrogen sulphide and forms the corresponding *carbanilide*, colourless, anhydrous needles or rods, m. p. 185—186° (from benzene), small, monohydrated needles, m. p. 155° after previous softening (from dilute alcohol). *Cupreine-5-thiooxazole*, microscopic needles which do not melt below 300°, is obtained as by-product of the action of phenylthiocarbimide on 5-aminocupreine or, more conveniently, by the direct action of carbon disulphide on the latter; it gives a *monosulphate*, red needles ($+4\text{H}_2\text{O}$), which is only stable in solution in the presence of an excess of acid.

5-Aminoquinine, m. p. 214—215°, $[\alpha]_D^{20} - 22.5^\circ$ (in alcohol), -119.3° (in ether), is obtained in small yield by the methylation of 5-aminocupreine by methyl sulphate or diazomethane. *5-Aminoethylcupreine* forms prismatic needles or plates, m. p. 213—214°, $[\alpha]_D^{20} - 21.5^\circ$ (in alcohol), -121.6° (in ether); the *platinichloride* ($+1\text{H}_2\text{O}$), darkening at about 195° and gradually decomposing at a higher temperature; the *monosulphate*, slender needles ($+3\text{H}_2\text{O}$), m. p. 183—184° (decomp.) after darkening at 173°, and the *disulphate*, red powder, m. p. 143° (decomp.) after darkening at 100°, are described. Reduction of aminoethylcupreine with hydrogen in the presence of palladium readily yields the *hydro-base*, m. p. 212°.

Sodium hydrocupreine-5-azobenzene-p-sulphonate is obtained in the same manner as the corresponding cupreine compound, to which it shows the closest resemblance; the corresponding *sulphonic acid* (+3H₂O) is also described. *5-Aminohydrocupreine* is an unstable substance which darkens above 100°, softens about 160°, and has m. p. 197° (on account of incipient decomposition the latter value is seldom observed, the m. p. usually being 180—185°); it has $[\alpha]_D^{20} -125.9^\circ$ (in ether), -24.0° (in alcohol); it gives a *monosulphate*, yellow needles, which darken at 180° and decompose without melting above 200°, and a *disulphate*, rust-red powder which decomposes above 160°. *5-Aminohydroquinine*, yellow needles, m. p. 217—218°, is obtained in the same manner as 5-aminoquinine, which it greatly resembles and from which it can be prepared by catalytic reduction; it has $[\alpha]_D^{20} -14.1^\circ$ (in alcohol), -120.6° (in ether). *5-Aminoethylhydrocupreine* forms intensely yellow crystals, m. p. 211—212°, $[\alpha]_D^{20} -123.8^\circ$ (in ether), -13.2° (in alcohol); when treated with ethyl chloroformate it yields amorphous ethylhydrocupreine ethyl urethane, m. p. 100—110°, $\alpha_D^{20} +14.8^\circ$.
H. W.

Diazo-reaction of Morphine. LUDWIG LAUTENSCHLÄGER (*Arch. Pharm.*, 1919, 257, 13—18).—Morphine and its salts couple with diazonium compounds in alkaline solution to yield dyes, the most suitable reagent being diazobenzenesulphonic acid. For qualitative work an approximately 2% aqueous solution of the latter is added to the solution of the morphine salt which is made alkaline with sodium carbonate or hydrogen carbonate; a deep red to pale red coloration, according to the concentration of the alkaloid, is immediately developed, which becomes orange after acidification with dilute acid. The limit of sensitiveness for the sodium carbonate solution is less than 1 in 10,000. The dye has little affinity for fibres in an acid bath.

Morphine is the only member of the opium alkaloids which yields a true dye with diazonium compounds; the synthetic derivatives of morphine (dionin, heroin, peronin) do not give the reaction, whilst of the commoner pharmacological alkaloids only a few give dyes. A table is given in the original showing the colorations yielded by morphine, emetine, sparteine, physostigmine, piperidine, coniine, and nicotine with diazobenzenesulphonic acid, diazotised arsanilic acid, 2:5-dichlorobenzenediazonium chloride, *p*-nitrobenzenediazonium chloride, and benzidine tetrazotate in alkaline solution.

The constitution of the morphine dyes remains undecided, but titration with titanous chloride shows that one and two molecules of morphine are contained in the diazo- and tetrazo-dyes respectively. Methyl- and ethyl-morphine do not give the reaction. The physiological action of morphine is destroyed by its conversion into the diazonium compound. Attempts to obtain an aminomorphine by reduction of the dye under varying conditions did not lead to the desired result.

The reaction can be used for the toxicological detection of morphine in the presence of its substituents and of other alkaloids.

Quantitative determinations show that morphine can be estimated as accurately by the colorimetric method with diazobenzene-sulphonic acid as by iodic acid or by Marquis's method; the method is most suitably applied to solutions containing 0.5—0.05 mg. of alkaloid per c.c., and has the advantage that it is not influenced by the presence of other opium alkaloids. A series of estimations of morphine in ripe poppy heads by the diazo- and iodic acid methods yielded identical results.

H. W.

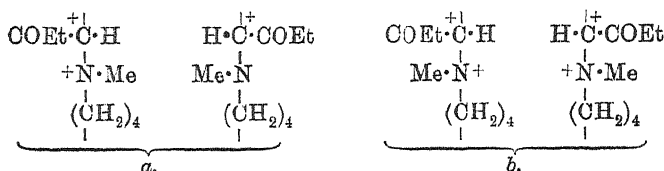
Oxydihydrocodeinone Hydrochloride [Eukodal]. MARTIN FREUND and EDMUND SPEYER (*Münch. med. Woch.*, 1917, **64**, 380—381; from *Chem. Zentr.*, 1919, i, 28—29).—Thebaine eliminates methyl alcohol when oxidised by hydrogen peroxide and passes into a tertiary base, $C_{18}H_{19}O_4N$, which contains only one methoxy-group and has ketonic properties; one hydrogen atom in thebaine is replaced by hydroxyl. The substance is related to codeinone, obtained by the oxidation of codeine, and, since it contains an additional atom of oxygen, is termed oxycodeinone. The aliphatic double bond in oxycodeinone is reduced by hydrogen, yielding *oxydihydrocodeinone* (annexed formula). The base crystallises in rods, m. p. 220—222°. The hydrochloride is a stable substance, freely soluble in water. The solution can be sterilised by heat without undergoing decomposition. The free base is precipitated in the crystalline form by addition of ammonia, sodium carbonate or hydroxide, and does not dissolve in an excess of alkali. Eukodal is used as a narcotic.

H. W.

The Alkaloids of the Pomegranate Tree. VI. The Relationship between Methylisopelletierine, *dl*-Methylconhydrinone, and *N*-Methylpiperidylpropan- α -one. An Instance of Isomerism with Substances containing an Asymmetric Tervalent Nitrogen Atom. KURT HESS (*Ber.*, 1919, **52**, [B], 964—1004).—It has been previously shown that methylisopelletierine is α -1-methylpiperidylpropan- α -one, and that it may be formed from conhydrine (*A.*, 1918, i, 35); a more extended examination of the latter reaction now proves that two bases are formed, one of which is identical with methylisopelletierine, whilst the other is *dl*-methylconhydrinone. Synthesis of α -1-methylpiperidylpropan- α -one leads to a product identical with the latter. The formation of methylisopelletierine from conhydrine is, however, shown not to be due to impurity in the latter, and further confirmation of the formula ascribed to it is obtained by its oxidation to α -methyl-

p*

piperidinecarboxylic acid and acetic acid. Since the two bases yield different oximes and hydrazones, their isomerism cannot be attributed to keto-enolic desmotropy, and the author is led to the conclusion that it is due to the presence of an asymmetric carbon atom and an asymmetric tervalent nitrogen atom in the molecule. The following formulæ are then possible:



(For convenience, the piperidine ring is represented as opened at one point and placed in the plane of the paper.) Owing to the relative readiness with which methylisopelletierine reacts with semicarbazide, the formula, *a*, is tentatively proposed for it. Unexpectedly, the isomerism is still preserved when the bases are converted into their methiodides, although this phenomenon does not appear to have been observed previously with quaternary ammonium salts of the type [NABCC]X; a similar case may, however, be presented by Willstätter's dihydroarecoline methiodide and the methiodide of methyl methylhexahydronicotinate (Hess and Liebbrandt, this vol., i, 220).

It has not been possible, up to the present, to cause the interconversion of methylisopelletierine and *dl*-methylconhydrinone.

[With FRÉD. A. EICHEL.]—Methylconhydrine (A., 1918, i, 35) has $[\alpha]_D^{20} - 42.27^\circ$ (in water), $[\alpha]_D^{20} - 39.42^\circ$ (in alcohol). *d*-Conhydrinone (*loc. cit.*) has $[\alpha]_D^{20} - 11.42^\circ$ in aqueous solution; it gives a *hydrobromide*, m. p. 146° after previous softening, a *picrate*, m. p. $91-92^\circ$, an *ethylurethane*, b. p. $133^\circ/15$ mm., and an impure *hydrazone*, b. p. $123-125^\circ/18$ mm., which yields a *picrate*, m. p. 164° after previous softening. Methylation of *d*-conhydrinone with methyl sulphate in the presence of alkali leads to a mixture of racemic methylconhydrinone and methylisopelletierine, the ultimate separation of which is accomplished by taking advantage of the fact that the latter readily reacts with semicarbazide, to which the former is indifferent. *dl*-Methylconhydrinone is a colourless oil, b. p. $95^\circ/15$ mm.; it gives a *hydrochloride*, needles, m. p. 124° after softening from 119° , a *picrate*, cubic crystals, m. p. 106° , a *hydrobromide*, slender needles, m. p. $137-138^\circ$ after previous softening, and an oily *oxime*, b. p. $158^\circ/22$ mm., which yields a *picrate* melting to a cloudy liquid at 118° and becoming transparent at about 145° . When *d*-conhydrinone is treated with methyl iodide, the *methiodide* of the tertiary base is produced; it forms prisms, m. p. 118° , $[\alpha]_D^{20} - 2.47^\circ$.

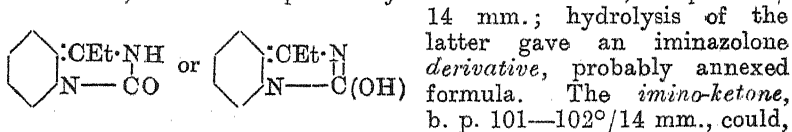
Attempts to methylate or oxidise ψ -conhydrine, under conditions which were found suitable for conhydrine, did not lead to a satisfactory result, the material being recovered unchanged.

[With H. MUNDERLOH.]— α -1-Piperidylpropan- α -ol is prepared by the catalytic reduction of α -ethylpyridyl ketone, and is obtained in two forms, m. p.'s 99—100° and 83—85° respectively, which, on methylation, yield α -1-methylpiperidylpropan- α -ols, b. p.'s 96—97°/14 mm. and 97—99°/1 mm. respectively. Oxidation of a mixture of the latter substances gives α -1-methylpiperidylpropan- α -one, b. p. 88—89°/12 mm., which is shown to be identical with *dl*-methylconhydrinone by an exhaustive examination of the picrate, hydrochloride, hydrobromide, and methiodide.

For purposes of comparison, a number of derivatives of methylisopelletierine has been prepared. The *hydrochloride* of the *dl*-base has m. p. 156° and decomposes at 160°; the *methiodide* forms cubic crystals, m. p. 156°; the *oxime* is a viscous oil, b. p. 160°/12 mm., which forms a *picrate* (or possibly mixture of picrates), m. p. 106°; the *methiodides* of the *d*- and *l*-bases also have m. p. 156°, but depression of the melting point is observed when they are mixed with the racemic form.

Methylisopelletierine is oxidised by chromic acid in sulphuric acid solution to *methylisopelletierinic acid*, which is shown to be identical with 1-methylpiperidine-2-carboxylic acid previously synthesised by Hess and Liebrandt (A., 1917, i, 354) in the form of its ethyl ester; the air-dried acid ($+\frac{1}{2}\text{H}_2\text{O}$) has m. p. 214—215° [*hydrochloride*, m. p. 205°; *platinichloride* ($+2\text{H}_2\text{O}$), m. p. 218—219° (decomp.)]; the *methiodide* of the ethyl ester crystallises in short rods, m. p. 129—131°; the *gold* salt of the methochlorides of the ethyl ester and of the acid have m. p.'s 88° and 254° (decomp.) respectively. The methiodide of ethyl 1-methylpipercolinate and some of its derivatives have previously been described by Willstätter; repetition of his work has, however, yielded products identical with those obtained from methylisopelletierine and differing in their physical constants from those described by him.

Attempts to demethylate methylisopelletierine by cyanogen bromide yielded *methylisopelletierine methobromide*, m. p. 134—136°, and the expected cyanamide derivative, b. p. 173°/14 mm.; hydrolysis of the

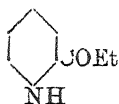


however, be obtained by treatment of methylisopelletierine with ethyl azodicarboxylate; it gives a *picrate*, m. p. 154°, a *hydrobromide*, slender needles, m. p. 149°, and a *hydrochloride*, m. p. 137—138°, after previous softening.

*iso*Pelletierine is not methylated by formaldehyde and formic acid, but is converted by methyl sulphate into methylisopelletierine; *dl*-methylconhydrinone does not appear to be formed in this reaction. Attempts to convert methylisopelletierine into *dl*-methylconhydrinone by treatment with acetic and hydrochloric acids at 200°, with glacial acetic acid at 110—120°, with alcohol at 105—115°

or with alcoholic sodium ethoxide solution yielded only unchanged material and resinous or oily products. H. W.

The Alkaloids of the Pomegranate Tree. VII. Natural Occurrence of *iso*Pelletierine. KURT HESS (*Ber.*, 1919, 52, [B], 1005—1013).—During the preparation of the large quantities of alkaloids required in the investigation of methyl*iso*pelletierine (pre-



ceding abstract), the author has observed the occurrence of *isopelletierine* (annexed formula) in small amount. The alkaloids are separated in much the same manner as previously described; after removal of ψ -pelletierine by freezing, and of the bulk of pelletierine as the hydrobromide, the residual material is distilled under diminished pressure, when considerable quantities of resin are left behind. The distillate is treated with ethyl chloroformate, and the product is repeatedly fractionated, when, after removal of α -1-methylpiperidylpropan- β -one and methyl*iso*pelletierine, a small fraction is obtained, b. p. 150—165°/13 mm., which consists of a mixture of the urethanes of pelletierine and *isopelletierine*. When hydrolysed with aqueous-alcoholic sodium hydroxide solution, the liberated pelletierine is resinified (the preparative regeneration of pelletierine from its urethane cannot be accomplished at present in spite of many variations in the conditions of the experiments), whilst the *isopelletierine* is unaffected and is obtained on distillation as an optically-inactive oil, b. p. 102—107°/11 mm. The picrate has m. p. 152° after previous softening, whereas that obtained from *isopelletierine* formed by demethylation of methyl*iso*pelletierine (preceding abstract) has m. p. 154° after previous softening; mixed m. p. 154°. The hydrobromides of the natural and synthetic bases and mixture of them melt at 149°.

The yields of the various alkaloids from 100 kilos. of the bark are approximately as follows: pelletierine, 52.5 grams; ψ -pelletierine, 179 grams; methyl*iso*pelletierine, 22 grams; *isopelletierine*, about 1.5 grams; α -1-methylpiperidylpropan- β -one, about 1 gram.

Owing to an error in calculation, the specific rotations of a number of salts of pelletierine and methyl*iso*pelletierine are incorrectly recorded in a previous paper (A., 1918, i, 404); the following are the accurate values: *d*-Pelletierine *d*-bitartrate, $[\alpha]^{20} + 21.00^\circ$, $[\alpha]^{21} + 20.93^\circ$; *l*-pelletierine *l*-bitartrate, $[\alpha]^{20} - 20.94^\circ$, $[\alpha]^{21} - 21.80^\circ$; *d*-pelletierine sulphate, $[\alpha]^{18} + 5.86^\circ$, $+ 6.11^\circ$; *l*-pelletierine sulphate, $[\alpha]^{18} - 5.89^\circ$; *d*-methyl*iso*pelletierine *d*-bitartrate, $[\alpha]^{20} + 22.77^\circ$; *l*-methyl*iso*pelletierine *l*-bitartrate, $[\alpha]^{18} - 20.83^\circ$ and $- 22.40^\circ$; *d*-methyl*iso*pelletierine sulphate, $[\alpha]^{18} + 7.64^\circ$, 8.53° ; *l*-methyl*iso*pelletierine sulphate, $- 8.03^\circ$; *d*-methyl*iso*pelletierine hydrochloride, $[\alpha]^{18} + 11.08^\circ$; *l*-methyl*iso*pelletierine hydrochloride, $[\alpha]^{18} - 10.64^\circ$. H. W.

Some Derivatives of Piperonaldehyde. RUDOLF WILKENDORF (*Ber.*, 1919, 52, [B], 606—616).—I. *Quinazoline derivatives*.—

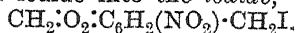
Piperonaldehyde is nitrated by dropping a concentrated acetic acid solution into well-cooled and agitated nitric acid (D 1.41), and then converted further into the oxime and reduced to *o*-aminopiperonaldoxime (Haber, A., 1891, 704). This is reduced by means of sodium amalgam and alcohol, the solution being maintained slightly acid by the addition of acetic acid, when 6-amino-3:4-methylenedioxybenzylamine is obtained as an oily base, which forms a *dihydrochloride*, bundles of long, sharp needles, decomp. 175—180°, and a yellow *mono-picrate*. When heated with sodium formate and anhydrous formic acid, the salt produces 6:7-

methylenedioxy-3:4-dihydroquinazoline, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2 \begin{smallmatrix} \text{CH}_2\cdot\text{NH} \\ \text{N}=\text{CH} \end{smallmatrix}$,

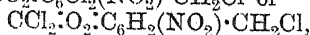
which crystallises in bitter needles, m. p. 153°, and forms a *hydrochloride*, bundles of needles, m. p. 267—268° (decomp.), an almost insoluble *picrate*, m. p. 234°, and an insoluble *platinichloride*, decomp. 235°. When oxidised by alkaline ferricyanide, the base yields 6:7-methylenedioxyquinazoline, m. p. 172—173° (after vacuum distillation), which gives a *picrate*, long, slender, pale yellow needles, m. p. 216°, and a *platinichloride*, decomp. 270—275°, and may be reduced by sodium amalgam to 6:7-methylenedioxy-1:2:3:4-tetrahydroquinazoline. This crystallises in glossy leaflets, m. p. 101°, and forms a *picrate*, terra-cotta-coloured tablets, m. p. 172—173° (decomp.).

The original base forms a *triacetyl* derivative, $\text{C}_7\text{H}_7\text{N}_2\text{Ac}(\text{OAc})_2$ or $\text{C}_7\text{H}_6\text{N}_2\text{Ac}_2(\text{OAc})\cdot\text{OH}$, bundles of slender needles, m. p. 200—201°, when shaken with acetic anhydride in the cold, but the *benzoyl* derivative, $\text{CH}_2:\text{O}_2:\text{C}_6\text{H}_2(\text{NH}_2)\cdot\text{CH}_2\cdot\text{NHBz}$, m. p. 255°, is obtained by the Schotten-Baumann method.

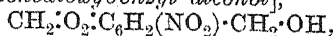
II. 6-Nitropiperonyl Alcohol.—6-Nitropiperonyl chloride (Robinson and Robinson, A., 1916, i, 167) does not react at all readily with potassium carbonate solution, and was therefore converted by means of sodium iodide into the *iodide*,



This crystallises in bundles of elongated, pale yellow needles, m. p. 97—98°, but it does not irritate the skin, as the chloride does, and fails to react with silver oxide. With the idea that the iodine atom may have wandered into a ring position, the substance was chlorinated, in the expectation that a compound of the type $\text{R}\cdot\text{ICl}_2$ would be formed. During the process, however, iodine is liberated, and ultimately a *dichloro-6-nitropiperonyl chloride* is formed, either $\text{CH}_2:\text{O}_2:\text{C}_6\text{Cl}_2(\text{NO}_2)\cdot\text{CH}_2\text{Cl}$ or



pale yellow needles, m. p. 139—140°. Both the chloride and the iodide react readily with sodium acetate in alcoholic solution to form the *acetate*, tablets, m. p. 150°, which may be hydrolysed by boiling with 20% sulphuric acid to 6-nitropiperonyl alcohol [6-nitro-3:4-methylenedioxybenzyl alcohol],



this forming pale yellow crystals, m. p. 121°. The corresponding *thiocyanate*, m. p. 88—89°, is obtained by the action of potassium

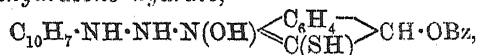
thiocyanate on the chloride in boiling alcohol, and may be converted by treatment with ammonium sulphide into *di-6-nitropiperonyl disulphide*, $[\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2(\text{NO}_2)\text{:CH}_2]_2\text{S}_2$, pale yellow needles, m. p. 103—104°. J. C. W.

Formation and Reactions of Imino-compounds. XIX. The Chemistry of the Cyano-acetamide and Guareschi Condensations. GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE (T., 1919, 115, 686—704).

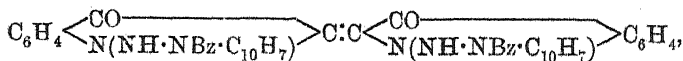
Nitration of Diphenylethylenediamine. GEORGE MACDONALD BENNETT (T., 1919, 115, 576—578).

New Derivatives in the Indole and Indigotin Groups. Isatin. III. AUGUST ALBERT and LEOPOLD HURTZIG (*Ber.*, 1919, 52, [B], 530—542. Compare A., 1915, i, 595; this vol., i, 99).—In the last paper, the behaviour of 1-oxy-2-thiol-3-benzoyloxy-3-hydroindole towards phenylhydrazine, and various reactions of the product, were described. Similar experiments with β -naphthylhydrazine are now recorded.

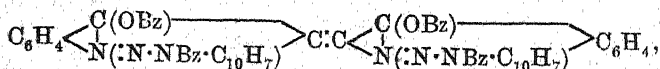
o-Nitrobenzaldehyde is converted into its cyanohydrin, from which the required material is obtained by benzoylating and then reducing with ammonium sulphide and shaking the thioamide with dilute hydrochloric acid. *2-Thiol-3-benzoyloxy-1:3-dihydroindole-1- β -naphthylhydrazone hydrate*,



forms colourless needles, m. p. 120—122° (fuses to a red liquid), and reacts with 0.5*N*-sodium hydroxide to give 1:1'-*bis- β -naphthylhydrazinoindigotin*, which crystallises in dark red, lanceolate needles, m. p. 228° (decomp.), gives a brown sulphate which is easily hydrolysed, and changes into the bluish-red salt of the enolic form when covered with concentrated sodium hydroxide. The presence of two carbonyl groups is revealed by the formation of a *bisphenylhydrazone*, bundles of pale yellow needles, m. p. 183°, and the *dihydrochloride* of a *di-anil*, wine-red needles, m. p. 202°. The *N:N'-dibenzoyl* derivative,



is obtained by boiling the indigotin with 10*N*-sodium hydroxide until it is completely changed into a bluish-red powder, and then shaking with benzoyl chloride in the cold; it forms sharp, yellow needles, m. p. 184°, and gives a yellow *bisphenylhydrazone*, $\text{C}_{62}\text{H}_{46}\text{O}_2\text{N}_{10}\text{.2H}_2\text{O}$, m. p. 140—142° (after some decomposition at 107°). A *tetrabenzoyl* derivative,



is formed if an excess of benzoyl chloride is employed; it crystal-

lises in red needles, m. p. 166°, and gives the above phenylhydrazone of the dibenzoyl derivative when warmed with phenylhydrazine.

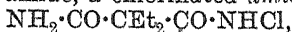
1:1'-Bis- β -naphthylhydrazinoindigotin suffers reduction by ammonium sulphide to indigotin, and by zinc dust and sodium hydroxide to 1:1'-diaminoindigotin, which is readily converted into indigotin-1:1'-imide. The acetyl derivative of this crystallises in bluish-violet needles, m. p. 212° (*loc. cit.*), and the oxime fuses and resolidifies at 290°. Reduction with zinc and acetic acid gives β -naphthylamine and the lactim form of isatin, for phenylhydrazine precipitates the α -phenylhydrazone, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \text{NH} \end{smallmatrix} C:N \cdot NHPh$ (Heller, A., 1907, i, 442).

J. C. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262).—The method depends on the action of hypohalogenites on C-C-arylalkylcyanoacetamides. Thus, the sodium compound of phenylecyanoacetamide reacts with ethyl iodide to form *phenylethylcyanoacetamide*, crystals, m. p. 116°, which is dissolved by sodium hypobromite solution and yields, after short warming, *phenylethylhydantoin*, small, shining needles, m. p. 201—202°. Phenylallylhydantoin is similarly prepared. The arylalkylhydantoins are useful soporifics.

H. W.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310426, additional to D.R.-P. 309508; from *Chem. Zentr.*, 1919, ii, 262. Compare preceding abstract).—The preparation is effected by the action of hypohalogenites on malonamide. Thus, diethylmalonamide and potassium hypobromite yield diethylhydantoin. *Phenylethylmalonamide*, prepared from phenylethylcyanoacetamide and concentrated sulphuric acid at 125°, forms small leaflets, m. p. 124° (decomp.), and is converted by sodium hypobromite after some hours into phenylethylhydantoin, m. p. 201°; if the solution is acidified immediately after solution of the amide, a chlorinated amide,



colourless needles, m. p. 152°, is obtained when hypochlorite is used. Diallylmalonamide yields C-C-diallylhydantoin, colourless needles, m. p. 204°.

H. W.

Reduction of the Nitrile Group. J. J. BLOCH (*J. Soc. Chem. Ind.*, 1919, 38, 118—120).—The author describes a series of unsuccessful attempts to reduce the nitrile group in 5-cyanomethylbenziminazole and 5-cyanomethyl-2-methylbenziminazole (Maron, Kontorowitsch, and Bloch, A., 1914, i, 684) to the amino-group. With sodium and alcohol, reduction proceeds mainly according to the scheme: $R \cdot CH_2 \cdot CN + Na + H = R \cdot CH_3 + NaCN$; with palladium hydrosol, with acetic acid and iron, sodium amalgam, aluminium amalgam, or zinc dust, only traces of base are obtained. The use of mineral acids causes hydrolysis of the nitrile. 2-Methyl-

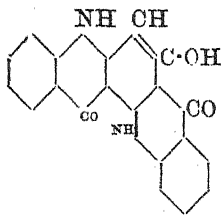
iminazolyphenylacetic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\langle\begin{smallmatrix} \text{N} \\ \text{NH} \end{smallmatrix}\rangle\text{CMe}$, has m. p. 218—219° (anhydrous), 117° (+2H₂O); the *mercuric* salt decomposes without melting at 230°.

Reduction of benzyl cyanide with sodium and alcohol gives phenylethylamine in 35—40% yield, the process being improved by the addition of toluene. Toluene, ammonia, methylamine, and sodium cyanide are always formed, the two main reactions being the normal reduction to the amine, and $\text{CH}_2\text{Ph}\cdot\text{CN} + \text{Na} + \text{H} \rightarrow \text{PhCH}_3 + \text{NaCN}$ (compare Johnson and Guest, A., 1909, i, 784).

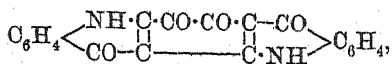
H. W.

Improvements in the Production of a Colouring Matter (*N*-Dihydro-1:2:2':1'-anthraquinone-azine). JAMES MORTON, ARTHUR GILBERT DANDRIDGE, and MORTON SUNDOUR FABRICS, LTD. (Brit. Pat., 126112).—The substitution of potassium chlorate for potassium nitrate in the preparation of *N*-dihydro-1:2:2':1'-anthraquinone-azine from 2-aminoanthraquinone by fusion at 250° with potassium hydroxide and an oxidising agent (see Brit. Pats., 3239, 22762 of 1901) results in an improved yield of dye of much greater purity, which dyes cotton to much brighter shades than can be obtained with the impure dye prepared by the older method. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] G. F. M.

Structure of Hydroxyquinacridone. WL. BACZYŃSKI and ST. VON NIEMENTOWSKI (*Ber.*, 1919, 52, [B], 461—484. Compare A., 1896, i, 261).—The hydroxyquinacridone obtained by the condensation of anthranilic acid with phloroglucinol might have either a linear structure like anthracene or an angular structure like phenanthrene. Decisive evidence has been very hard to find, but the authors are now able to show that the annexed, angular, or “ β ” structure is correct, which is in keeping with the results of many other syntheses of quinoline derivatives with at least three nuclei.



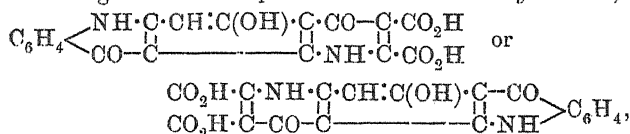
In the first place, the condensation product of phloroglucinol with *o*-aminobenzaldehyde was shown to be 4-hydroxy- β -quinacridone, because it could be oxidised to a diketone which condensed with *o*-phenylenediamine, and was therefore an *o*-diketone. Similarly, hydroxyquinacridone may be oxidised by boiling with chromic and acetic acids, or 6% nitric acid, to *diketo- β -quinacridone*,



which is a microcrystalline, red powder, m. p. 374° (decomp.), sparingly soluble in boiling quinoline or nitrobenzene, freely soluble in concentrated sulphuric acid, from which it may be precipitated again by dilution, otherwise insoluble. Unfortunately, it does

not react in the desired way with *o*-phenylenediamine, this reagent usually causing reduction to dihydroxy- β -quinacridone (see below). It does react with aniline, however, giving two *anils*, $C_{20}H_{15}O_3N_3 \cdot 3H_2O$, one soluble in ethyl acetate, forming almost black crystals, m. p. 210—230°, and an insoluble one, also black, m. p. 320°.

Oxidation with nitric acid was then tried, with the idea of obtaining recognisable degradation products, but the results were confused by the readiness with which nitration takes place. Boiling the original compound with an acid of D 1.2 gives an 80% yield of a *nitrohydroxy- β -quinacridone*, crystallising from boiling nitrobenzene in chestnut-brown needles, m. p. 330°. If the diketone is boiled with an acid of D 1.12, it gives a *nitrodiketo- β -quinacridone*, which is best obtained from the above nitrohydroxy-compound by oxidation with chromic acid; it crystallises from nitrobenzene in yellow filaments, m. p. 340° (decomp.). A *dinitrodiketo- β -quinacridone*, $C_{20}H_8O_8N_4 \cdot H_2O$, orange leaflets, m. p. 200°, is obtained if the diketone-compound is boiled with an acid of D 1.2. When the hydroxyquinacridone is boiled with 6% nitric acid (D 1.033), the main product is the diketone-derivative (above), but small quantities of a dibasic acid are formed as well. This gives the fluorescein reaction with resorcinol, and is therefore an *o*-dicarboxylic acid, formed by the destruction of one of the outside rings. *Benzo-m-phenanthrolinecarboxylic acid*, as it is called,



crystallises from acetone in pale yellow needles, m. p. 283° (decomp.), forms a *silver* salt, H_2O , a pale yellow *barium* salt, $3H_2O$, and a dark brown *compound*, decomp. 160—170°, of the formula, $\begin{array}{c} CO \cdot C_{10}H_8O_3N_2 \\ O - C[C_6H_8(OH)_2]_2 \end{array}$, when fused with resorcinol.

Better results in the oxidative degradation of the compound were obtained with permanganate. If the hydroxyquinacridone is suspended in water and gradually mixed with a saturated solution of permanganate, it is oxidised to a dibasic acid, *quinacridonic acid*, $C_6H_4 \begin{array}{c} \text{NH} \cdot C \cdot CO_2H \quad CO_2H \cdot C \cdot CO \\ \text{CO} - C \text{-----} C \cdot NH \end{array} > C_6H_4$ (or its tautomeride),

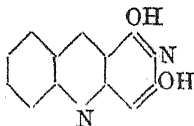
which is a white, microcrystalline powder, becoming orange at 240—255°, soft at 375°, and molten at 385°. It forms an *ammonium* salt, a *barium* salt, $3H_2O$, an *ethyl hydrogen* salt, almost white nodules, m. p. 240° (decomp.), an *ethyl ester*, canary-yellow, hexagonal tablets, m. p. 417° (corr.), and an *anhydride* (by heating at 300°), crystallising in tufts of white needles, m. p. 437° (decomp.). When heated with hydrochloric acid in a sealed tube, it yields 4:4'-*dihydroxy-3:2'-diquinolyl*, in very slender needles, m. p. 430°, which dissolves in ammonia and alkali hydr-

oxide solutions with intense blue fluorescence, and is also soluble in the more concentrated solutions of hydrochloric acid. The potassium salt, $6\text{H}_2\text{O}$, is obtained when a solution containing 1 part in 120 parts of boiling 20% potassium hydroxide is cooled. The chief evidence in the whole argument is the fact that this dihydroxy-compound or the quinacridonic acid yields the known 3:2'-diquinolyl, $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CH} \\ \text{CH}:\text{C} \end{array} \text{---} \begin{array}{c} \text{CH}:\text{CH} \\ \text{C}=\text{N} \end{array} \text{C}_6\text{H}_4$, when distilled with zinc dust.

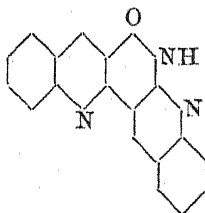
The manganese dioxide sludge obtained in the oxidation of the hydroxyquinacridone with permanganate contains unchanged material and the diketoquinacridone. The latter is easily reduced by sulphurous acid in this condition (not so when previously isolated and dried), and the dihydroxy- β -quinacridone so formed can be extracted with alcoholic potassium hydroxide; it crystallises in brownish-yellow granules, decomp. 425° .

Various products are obtained by the action of potassium hydroxide on 4:5-diketo- β -quinacridone. Boiling with alcoholic solutions gives quinacridonic acid; prolonged boiling with 2.5% aqueous solutions produces the pale yellow diquinolonyleneglycollic acid, $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH}\cdot\text{C}\cdot\text{C}(\text{OH})(\text{CO}_2\text{H})\cdot\text{C}\cdot\text{C} \\ \text{CO}\cdot\text{C} \end{array} \text{---} \begin{array}{c} \text{C}\cdot\text{NH} \\ \text{C}\cdot\text{NH} \end{array} \text{C}_6\text{H}_4$, which loses carbon dioxide on heating and changes into diquinolonylenecarbinol, orange-red needles, m. p. $456\text{--}459^\circ$ (potassium salt, red needles, with $2\text{H}_2\text{O}$). J. C. W.

Syntheses of 1:3-Dihydroxybenzo-2:5-naphthyridine [1:3-Dihydroxy-2:5-naphthadiazine] and a New Angular System of Five Nuclei, namely, Diquinopyridone. ST. VON NIEMENTOWSKI and ED. SUCHARDA (*Ber.*, 1919, 52, [B], 484—492).—The condensation of *o*-aminobenzaldehyde with 2:4:6-trihydroxypyridine or glutazine differs somewhat from the reaction given by anthranilic acid (A., 1917, i, 477). Besides the expected 1:3-dihydroxy-2:5-naphthadiazine (I), there is also formed a new pentacyclic compound, "diquinopyridone" (II). The former is



(I.)

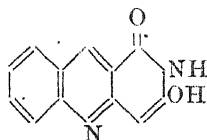


(II.)

practically insoluble in glacial acetic acid, but readily soluble in alkali hydroxides, whereas conditions are reversed in the case of the second compound.

1:3-Dihydroxy-2:5-naphthadiazine (called "1:3-dihydroxybenzo-2:5-naphthyridine") crystallises in scarlet, needle-like aggre-

gates of small prisms, m. p. 375° (decomp.), and forms a yellow *hydrochloride*, $0.5\text{H}_2\text{O}$, a mono-*acetyl* derivative, glistening, golden-yellow, rectangular plates, m. p. 350° (decomp.), a mono-*benzoyl* derivative, very thin, long, golden-yellow needles, with 1AcOH , m. p. 295° (decomp.), and a *p-nitrobenzeneazo*-compound, brownish-yellow needles, m. p. 360° (decomp.). It is decomposed by heating with hydrochloric acid in a sealed tube into 2-methylquinoline and 2-methylquinoline-3-carboxylic acid, and by boiling with 25% sodium hydroxide into 3-carboxyquinolyl-2-acetic acid (?),



$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_5\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.
Because of its deep red colour and its behaviour towards acyl chlorides and hydrolytic agents, the compound may probably have a quinonoid configuration (annexed formula).

Diquinopyridone (II) crystallises in pale straw-yellow needles, m. p. $312\text{--}314^{\circ}$, and forms a *dihydrochloride*, but no acyl derivatives.
J. C. W.

Vat-like Reduction Products of the Triphenylmethane Dyes. HEINRICH WIELAND (*Ber.*, 1919, 52, [B], 880—886. Compare this vol., i, 99).—The basic triphenylmethane dyes are readily reduced by sodium hyposulphite in aqueous-alkaline solution to colourless salts, which are re-oxidised to the dyes with extraordinary rapidity by air; the property is shared by the acid dyes such as aurin, the phthaleins, and fluorescein, which, however, are somewhat more slowly attacked by the alkaline reducing agent. The pure *sodium* salts have been isolated in the cases of crystal-violet and malachite-green, and appear to be derived from the triarylmethanesulphinic acids or the isomeric sulphoxylic esters; apparently, the first stage of the reaction consists in the addition of $\cdot\text{SO}_2\text{Na}$ groups at either end of the quinonoid system, followed by the elimination of sulphur dioxide and sodium chloride. When the sulphinates are heated with an excess of alkali, the solutions lose their autoxidisability; in the case of the basic dyes, the leuco-base is precipitated, whilst the solution derived from the acid dyes contains the leuco-compound. The sulphinic group is eliminated as sulphite. The course of the autoxidation has not been definitely elucidated; the main portion of the sulphoxyl group is removed as sulphite, and the precipitate which is formed contains considerable quantities of carbinol, which, however, is not a primary product of the change.
H. W.

Pyrimidines. ADELHEID VON MERKATZ (*Ber.*, 1919, 52, [B], 869—880).—2:4:6-*Trichloro-5-ethylpyrimidine*, plates or long rods, m. p. $75\text{--}77^{\circ}$, is prepared by the action of phosphoryl chloride on *sodium ethylbarbiturate* ($+2\text{H}_2\text{O}$ from aqueous solution); it is converted by concentrated alcoholic ammonia at the ordinary temperature into 2:6-*dichloro-4-amino-5-ethylpyrimidine*, needles, m. p. $214\text{--}216^{\circ}$. Fuming hydriodic acid reduces the

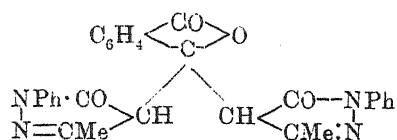
latter substance to 6-iodo-4-amino-5-ethylpyrimidine hydriodide, m. p. 204—206°. The corresponding base forms small needles, m. p. 191—193°, and yields a crystalline *hydrochloride*, *platinichloride*, and *aurichloride*; when treated with zinc dust and water, it gives the zinc double salt of 4-amino-5-ethylpyrimidine, needles, m. p. 233—235°; the free base has m. p. 163° and yields crystalline *auri-* and *platinichlorides*. The presence of the amino-group in position "4" in the pyrimidine ring follows from the non-identity of the compound with 4:6-dichloro-2-amino-5-ethylpyrimidine, which is synthesised in the following manner. Guanidine is condensed with ethyl ethylmalonate to form 2-amino-4:6-dihydroxy-5-ethylpyrimidine, which is converted by phosphoryl chloride into 4:6-dichloro-2-amino-5-ethylpyrimidine, needles, m. p. 191—192°; the latter is reduced by zinc dust to 2-amino-5-ethylpyrimidine, m. p. 142—143°, which forms double salts with mercuric, gold, and platinic chlorides. 6-Chloro-2:4-diamino-5-ethylpyrimidine is prepared by the action of alcoholic ammonia on 2:4:6-trichloro-5-ethylpyrimidine or 4:6-dichloro-2-amino-5-ethylpyrimidine; it forms plates, m. p. 183° (the *hydrochloride*, needles, the *platinichloride*, yellow octahedra, and the *picrate* are described), and is reduced by hydriodic acid and phosphorus to 2:4-diamino-5-ethylpyrimidine, m. p. 149—151°. 4:6-Diamino-5-ethylpyrimidine forms double pyramids, m. p. 233—235°; the *hydrochloride*, *nitrate*, long needles, *aurichloride*, small, yellow needles, and *platinichloride*, yellow rods, are described. 2:4:6-Triamino-5-ethylpyrimidine, m. p. 190° (corr.), is obtained from 2:4:6-trichloro-5-ethylpyrimidine and alcoholic ammonia at 210°, and is most readily purified by means of the *nitrate*; it separates from water + 1H₂O, gives a readily soluble *hydrochloride*, C₈H₁₁N₅.2HCl, a *platinichloride*, yellow needles, an *aurichloride*, minute needles, and a crystalline *picrate*.

The action of an alcoholic solution of sodium methoxide on 2:4:6-trichloro-5-ethylpyrimidine leads to the successive replacement of the three chlorine atoms by the methoxy-group, whereby (probably) 2:6-dichloro-4-methoxy-5-ethylpyrimidine, small needles, m. p. 55—57°, 6-chloro-2:4-dimethoxy-5-ethylpyrimidine, long, colourless needles, m. p. 33—34°, and 2:4:6-trimethoxy-5-ethylpyrimidine, slender needles, m. p. 67—68° (crystalline salts with gold, platinic, and mercuric chlorides), are formed. The constitution of the second of these substances follows from its reduction to 2:4-dimethoxy-5-ethylpyrimidine, b. p. 234—236° (corr.) (the *aurichloride* and *platinichloride* salts are crystalline), and demethylation of the latter to 5-ethyluracil, m. p. 300—303° (decomp.).

Attempts to prepare derivatives of 4-phenyl-6-methylpyrimidine by the condensation of benzoylacetone with carbamide did not lead to the desired result; by using thiocarbamide, however, the thiolpyrimidine was readily prepared, in which the mercapto-group was replaced by the hydroxy-group by treatment with dilute aqueous-chloroacetic acid solution in accordance with the directions of Wheeler and Liddle (A., 1908, i, 692); it is interesting to note

that the thioglycollates, assumed by these authors to be formed as intermediate products, are actually isolated in the present instance. 2-Thiol-4-phenyl-6-methylpyrimidine forms amber-coloured rhombs, m. p. 199—200°; 4-phenyl-6-methylpyrimidine-2-thioglycollate has m. p. 85°; 2-hydroxy-4-phenyl-6-methylpyrimidine crystallises in yellow needles, m. p. 228—229° (*hydrochloride*, long needles; *picrate*, crystalline aggregates; *platinichloride*, granular; *aurichloride*, small needles). 2-Chloro-4-phenyl-6-methylpyrimidine has m. p. 50—51° (*hydrochloride*, colourless needles); it is reduced by hydriodic acid and red phosphorus to 4-phenyl-6-methylpyrimidine, m. p. 44—45° (*hydride*, yellow crystals; the *aurichloride*, *platinichloride*, and *picrate* are crystalline). H. W.

Condensation of 1-Phenyl-3-methylpyrazol-5-one with Anhydrides. SARAT CHANDRA CHATTERJEE and ANANDA KISHORE DAS (*J. Amer. Chem. Soc.*, 1919, **41**, 707—709).—Antipyrine condenses with phthalic anhydride



(2 mols. to 1) at 180° to form a compound of the annexed formula, which crystallises in bright red needles, m. p. 212°. Succinic anhydride at 165° gives a similar compound, m. p.

184°. Benzoic and camphoric anhydrides give no definite products.

J. C. W.

Condensation Products from Amine Salts, Formaldehyde, and Antipyrine. C. MANNICH and B. KATHER (*Arch. Pharm.*, 1919, **257**, 18—33. Compare Mannich and Krösche, *A.*, 1913, **i**, 101).—Antipyrine and formaldehyde react readily with the salts of secondary and primary, but not of tertiary, amines in aqueous solution, forming salts in which the hydrogen atom attached to the 4C-atom of antipyrine is replaced by the methyl group. (For the radicle, $-\text{CH}_2\cdot\text{C}_{11}\text{H}_{11}\text{ON}_2$, the nomenclature antipyrinomethyl- is proposed.) Direct condensation between formaldehyde and antipyrine can frequently be completely prevented or hindered by addition of a small quantity of pyrimidone to the mixture. The substances behave similarly to those obtained from ammonium chloride, and are decomposed into the constituents by sulphurous acid. The new bases are somewhat closely allied to pyrimidone, but, however, do not show any antipyretic action. Their formation appears to depend on the mobility of the hydrogen atom influenced in antipyrine by the proximity of the double bond and the carbonyl group; attempts to obtain similar derivatives from substances similarly constituted in this respect failed in the cases of 1-phenyl-3-methylpyrazol-5-one, 1-phenyl-5-methylpyrazol-3-one, dimethylaniline, and barbituric acid, but succeeded with malonic acid and its monoalkyl derivatives and with 1-phenyl-2:5-dimethylpyrazol-3-one. The following individual substances are described:

antipyrinomethyldimethylamine, $\begin{array}{c} \text{NPh} \cdot \text{CO} \\ \diagdown \quad \diagup \\ \text{NMe} \cdot \text{CMe} \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{NMe}_2$, small

prisms, m. p. 93—94°, which do not yield the colour reactions of antipyrine, and are decomposed into other components by boiling dilute hydrochloric acid (10%) or by sulphurous acid; *hydrochloride*, fine needles, m. p. 208°. *Bisantipyrinomethylmethylamine*, $\text{NMe}(\text{CH}_2 \cdot \text{C}_{11}\text{H}_{11}\text{ON}_2)_2$, needles (+ 2H₂O), m. p. 111°. *Antipyrinomethyldiethylamine*, short prisms, m. p. 68°. *Bisantipyrinomethylethylamine*, slender needles, m. p. 143°. *Bisantipyrinomethylallylamine*, shining prisms, m. p. 163° (the base unites with two atoms of bromine in chloroform solution, but the product is not crystalline). *Ethyl bisantipyrinomethylaminoacetate*, needles grouped in rosettes, m. p. 174°. *Bisantipyrinomethyl-ac-tetrahydro-β-naphthylamine*, small, shining leaflets, m. p. 217°. *Antipyrinomethylpiperidine*, plates, m. p. 99°. *Antipyrinomethyltetrahydroquinoline*, slender needles (+ 1H₂O), m. p. 153°. *Bisantipyrinomethyl-ω-aminoacetophenone*, slender needles, m. p. 93°; *hydrochloride*, small leaflets, m. p. 96°. *Tetra-antipyrinomethylethylene-diamine*, shining prisms, m. p. 179°. *Bisantipyrinomethylpiperazine*, m. p. 248° (prisms + 4·5H₂O). *Antipyrinomethylmethyl-aniline*, small prisms, m. p. 140°. *isoAntipyrinomethyldimethylamine*, $\begin{matrix} \text{NPh} \cdot \text{OMe} \\ \text{NMe} - \text{CO} \end{matrix} > \text{C} \cdot \text{CH}_2 \cdot \text{NMe}_2$, small prisms (+ 1H₂O), m. p. 66°.

Condensation products could not be isolated from antipyrine, formaldehyde, and hydrazine hydrochloride or guanidine hydrochloride respectively.

H. W.

Preparation of Monoazo-dyes. FARBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 309951; from *Chem. Zentr.*, 1919, ii, 179).—Diazotised 5-nitro-2-aminobenzamides, in which the two hydrogen atoms of the amino-group are replaced by alkyl, aryl, or aralkyl groups, are coupled with the sulphonic acids of β-naphthylamine or its derivatives in acid solution. The products dye wool in red to violet shades from an acid bath, and the dyes are fast to light and rubbing. The nitro-2-aminobenzamides are obtained by the action of secondary aliphatic or aromatic amines on nitroisatoic acid. The following individual members are described: 5-nitro-2-aminobenz-methylanilide, m. p. 183—184°; 5-nitro-2-aminobenzethylanilide, m. p. 144—145°; 5-nitro-2-aminobenzdimethylamide, m. p. 213—214°; 5-nitro-2-aminobenzpiperidide, m. p. 163—164°; 5-nitro-2-aminobenzethyl-*o*-toluidide, m. p. 147—148°. H. W.

Formation of Diazoamino-compounds from β-Naphthylamine. GEORGE MARSHALL NORMAN (T., 1919, 115, 673—679).

Extension of the Theory of Isoelectric Point. Competitive Action of other Ions with H⁺ and OH⁻ Ions in the Precipitation of Denatured Albumins. LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1919, 94, 225—239).—The coagulation of denatured albumins is dependent on the hydrogen-ion concentration. Salts may exert a two-fold action. First, it is shown that other ions than H⁺ and OH⁻ ions may exert an influence on the process. In general, anions displace the optimal hydrogen-ion concentration for flocculation towards the acid side, whereas cations

exert an opposite effect. The action of the ions is in accordance with the ionic series. Secondly, there may be an inhibition or strengthening of the maximal precipitation at the isoelectric point, as compared with the maximum precipitation in the absence of salts. The earths exert the strongest inhibitory influence, that of the alkalis being less, whilst the heavy metals bring about the reverse effect. Of the anions, chlorine and bromine inhibit, whereas the iodine and CNS ions do not. These actions are a result of a competitive process between other ions and the H^+ and OH^- ions for the protein, which can bind or adsorb them in different amounts. Further knowledge must be based on a systematic investigation of the adsorption of ions by simple adsorbents. J. C. D.

Lysine as a Hydrolytic Product of Hordein. CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1919, **33**, 63—66).—Analyses of hordein by the method of Van Slyke indicate that the basic amino-acids are present in the following proportions: cystine 1.18%, arginine 2.82%, histidine 2.27%, and lysine 0.89%. The free amino-nitrogen present in this protein corresponds with one half the lysine nitrogen.

These values agree with those representing the distribution of the basic amino-acids in gliadin from wheat. J. C. D.

Casein. L. A. MAYNARD (*J. physical Chem.*, 1919, **23**, 145—153).—The author has repeated and confirmed the work of Plimmer and Bayliss (A., 1906, i, 325) on the action of 1% sodium hydroxide on casein. It is also shown that the phosphorus of the casein molecule is split off and changed into a soluble inorganic form by the action of 1% sodium hydroxide at 25° for long periods of time. At the same time, the loosely combined sulphur is also split off. On the addition of acids to the sodium hydroxide digest at the end of the digestion, a white precipitate is obtained which, although not identified, has been examined with reference to its dissimilarity from casein. It exhibits colloidal properties similar to those of casein as regards its behaviour with acids and bases. It responds to the various protein tests in the same way as casein, and is similarly precipitated by salts. Its solubility in various reagents is markedly different from that of casein, and a solution in lime-water is quite different from a similar solution of casein. When phosphoric acid was introduced into a lime-water solution, in such a way as not to destroy the colloidal solution, a milky solution was obtained which, on heating, behaved in the same way as a lime-water solution of casein. This reaction furnishes evidence in support of the hypothesis that the white colour of milk is due to the peptisation of calcium phosphate by the colloids in the milk. Attempts to cause this substance to adsorb phosphoric acid were unsuccessful, but the experiments do not necessarily show that such a combination is not present in casein, for both sulphur and albumoses are also split off by sodium hydroxide, and it may be that their presence is essential for the adsorption of phosphorus. J. F. S.

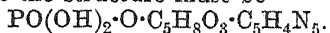
Hæmocyanin. I. Reduction of Oxyhæmocyanin by Physical and Biological Means. FILIPPO BOTTAZZI (*J. Physiol. Pathol. gén.*, 1919, 18, 1—7).—According to Alsberg and Clark (A., 1915, i, 67), oxyhæmocyanin of *Limulus* scarcely gives up any oxygen in a vacuum. The author finds this to be the case for *Octopus* blood, unless it is exposed in thin layers to a very high vacuum, when it is slowly, but completely, decolorised by loss of oxygen. This reduction is also effected by the living leucocytes, even if they are collected as a deposit by centrifuging. If the leucocytes are killed by acids, chloroform, ether, formalin, or are completely removed after centrifuging, the blood remains blue.

G. B.

An Optically Inactive Sodium Nucleate. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, 104, 189—210).—The preparation of a sodium salt of thymus-nucleic acid is described which is optically inactive and will not gelatinise. On the addition of acids, the activity and power of gelatinisation return, and the changes are reversible. The acid groups which hold the sodium in the alkaline salt must be very weak, for the addition of carbon dioxide or acetic acid results in the formation of the active salt. A number of observations are recorded which indicate that the structural changes which underlie the changes in physical properties may occur without corresponding changes in the degree of dissociation of the weak acid groups. It is suggested that these groups are not free in the active molecule, but that they are bound in a form which is sensitive to alkalis, acids, or rise in temperature.

J. C. D.

Adenine Mononucleotide. WALTER JONES and R. P. KENNEDY (*Journ. Pharm. Exp. Ther.*, 1919, 13, 45—53. Compare this vol., i, 294).—When a neutral or faintly alkaline solution of nucleic acid is oxidised with potassium permanganate, the various groups are destroyed in a definite order, and a residue is obtained from which no cytosine, uracil, or guanine can be isolated after acid hydrolysis. From this residue, an adenine mononucleotide has been isolated crystallising in needles, and giving rise to a crystalline brucine salt, m. p. 173—174°. On the grounds that the nucleotide is a dibasic acid and that it yields adenine on mild acid hydrolysis at a much more rapid rate than it does phosphoric acid, it is concluded that the structure must be



This formula is in accordance with everything that is known of the substance.

J. C. D.

The Effect of Hydrogen Ion Concentration on the Liquefaction of Gelatin. HARRISON E. PATTEN and ALFRED J. JOHNSON (*J. Biol. Chem.*, 1919, 38, 179—190).—The setting of gelatin is influenced by the hydrogen-ion concentration of the medium, and unless the gelatin is destroyed, this effect is probably reversible.

Gelatin in the concentrations used is not without effect on the buffer solutions, displacing the p_H in such a manner as would be expected from an aggregate of amino-acids acting amphotERICALLY.

J. C. D.

New Theories of the Formation and Action of Diastase.

J. WOHLGEMUTH (*Biochem. Zeitsch.*, 1919, **94**, 213—224).—The author cannot confirm the work of Biedermann (A., 1916, i, 62), who found a diastatic action in boiled starch solution. He is also unable to confirm the experimental results of Woker (A., 1916, i, 61, 447), who claimed that formaldehyde could exert a diastatic action. The severe criticisms of the latter author's work advanced by Kaufmann (A., 1916, i, 62) are supported. A quantitative recovery of starch may be effected after treatment with formaldehyde for twenty-four hours if the aldehyde is removed by phenylhydrazine and alcohol. The starch so recovered gives the typical reactions. The action of the formaldehyde must be, as Kaufmann suggested, due to a combination with the groupings which react with iodine.

J. C. D.

Fixation of Formaldehyde by Enzymes. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, **94**, 69—77).—The fixation of formaldehyde by emulsin was studied quantitatively, and from the amount found, assuming that combination of the aldehyde and free amino-groups in the emulsin occurs, it is estimated that 4% of the enzyme is represented by such groups in a reactive state. Previous experiments (A., 1915, i, 1018) gave a lower percentage, but this may be due to differences in the purity of the two preparations. The author interprets these and other results as evidence that emulsin possesses a protein nature.

J. C. D.

Biochemical Synthesis of Cellobiose by means of Emulsin.

EM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1919, **168**, 1016—1019).—From the residue left, after extracting gentiobiose and the mono- and di-glucosides of ethylene glycol obtained in the action of emulsin on a mixture of ethylene glycol, dextrose, and aqueous alcohol (see this vol., i, 137), the authors have now isolated and characterised cellobiose.

W. G.

Oxidising Enzymes. I. The Nature of the "Peroxide" Naturally Associated with certain Direct Oxidising Systems in Plants. MURIEL WHELDAL ONSLOW (*Biochem. J.*, 1919, **13**, 1—9).—If the tissues of certain plants (pear, potato, apple, and greengage) which give direct oxydase reactions are extracted with alcohol, something is removed which is part of the system responsible for the reactions. An aqueous extract of the alcohol insoluble fraction will not darken on exposure to air, nor will it give a blue coloration with guaiacum tincture until hydrogen peroxide is added. If these aqueous extracts, which contain the peroxydase, are treated with catechol or protocatechuic acid, they

darken on exposure and will give the guaiacum reaction. The pear oxydase added to a crude solution of caffeic acid, followed by guaiacum tincture, gave a blue colour. There is reason to believe that the tissues of all plants which turn brown on injury and give the direct reaction with guaiacum will behave in the same manner with catechol and subsequently towards guaiacum. Tissues of plants which normally do not give the direct oxydase reactions failed to yield extracts which oxidised catechol. It is possible that tannin may exert an inhibitory action in some cases. A substance is extracted from pears and potatoes by hot alcohol which is precipitated by lead acetate, is soluble in ether, and gives the reaction with ferric chloride and sodium carbonate characteristic of the orthodihydroxy-grouping of catechol.

The direct oxydases of plants prepared by precipitation of the expressed juices with alcohol have been termed laccases, but it appears probable that these complexes are precipitates containing the crude peroxydase and, in addition, the oxidised aromatic substance in an adsorbed condition. The conception of the oxydase system as formulated by Bach and Chodat is extended. The direct oxydase system in the pear fruit and potato tuber is due to the presence of peroxydase and an aromatic substance, giving reactions characteristic of the catechol grouping. On injury, the peroxydase activates the oxidation of the aromatic substance, with the formation of a peroxide. The peroxide-peroxydase system so formed will then give a blue coloration with guaiacum.

J. C. D.

Physiological Chemistry.

Non-protein Nitrogen of Human Blood. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, **94**, 84—128).—A detailed discussion of the significance of variations in the non-protein nitrogen of the blood, with especial reference to pathological conditions.

J. C. D.

Formation of Glycogen and Sugar at the Expense of Fats. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 689—691; from *Chem. Zentr.*, 1919, i, 113).—The author's experiments, since 1888, with the marmot lead him to the conclusion that sugar and glycogen can be formed directly from fats and indirectly from proteins.

H. W.

The Fat-soluble Accessory Substance. I. Its Nature and Properties. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 81—94).—The fat-soluble accessory growth-promoting factor as present in animal fats is not as stable to high temperatures as has

been assumed. The growth stimulating action of the factor present in butter and whale oil may be destroyed by exposure to a temperature of 100° for as short a time as one hour. Lower temperatures may cause destruction, but the process is not so rapid. In the case of whale oil, exposure to 37° for several weeks was found to cause a great deterioration in the amount of the accessory factor present. As far as could be ascertained, this was not due to changes of an oxidative or hydrolytic nature. The vitamine is not extracted from oils by water or dilute acids, but it may be partly removed by extraction with alcohol. Saponification of oils containing the accessory factor, even when conducted at the ordinary temperature and in the absence of water and oxygen, results in disappearance of the growth-stimulating properties. Fat-soluble *A* could not be identified with any known components of fats or with substances frequently associated with fats, such as cholesterol, phosphatides, or pigments. It is suggested that the vitamine may be an ill-defined body resembling an enzyme. J. C. D.

The Fat-soluble Accessory Factor. II. Its Rôle in Nutrition and Influence on Fat Metabolism. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 95—102).—The fat-soluble vitamine is necessary for maintenance of health in the adult, although for this purpose relatively smaller quantities are required than are necessary for growth and well-being in the young. No obvious pathological lesion has been observed to be a specific result of a deficiency of this accessory factor, but animals so deprived show a very much impaired resistance to bacterial invasion. No direct connexion between the fat-soluble *A* and fat metabolism could be traced. Absorption of fat or fatty acids from the intestinal tract is good, even when the animals are showing a decline in health as a result of the deficiency of this vitamine. J. C. D.

Rôle of the Antiscorbutic Factor in Nutrition. JACK CECIL DRUMMOND (*Biochem. J.*, 1919, **13**, 77—80).—The dietary requirements of the higher animals include, in addition to a satisfactorily balanced ration of proteins, fats, carbohydrates, and mineral salts, an adequate supply of three accessory food factors: (i) fat-soluble *A*; (ii) water-soluble *B*; (iii) the antiscorbutic factor, or water-soluble *C*. This confirms the results of Harden and Zilva (this vol., i, 186). J. C. D.

- * **Is Lactalbumin a Complete Protein for Growth?** A. D. EMMETT and G. O. LUROS (*J. Biol. Chem.*, 1919, **38**, 147—159).—Lactalbumin is a complete protein in the sense that it is not lacking in any essential nitrogenous cleavage product necessary for growth. Under some conditions, however, diets containing lactalbumin as a sole source of protein do not permit good growth in rats (see also McCollum, A., 1919, i, 186). This is explained by assuming that lactalbumin is either sensitive to certain toxic sub-

stances or that it is a protein unable to adsorb a vitamine other than water-soluble *B*. Lactose added to such unsatisfactory diets has a good effect, which may be due either to its power of overcoming the toxic agent, or to it carrying a water-soluble vitamine other than water-soluble *B*. J. C. D.

The Retention Power of the Kidney for Dextrose. Can the Calcium in the Perfusion Fluid be Replaced by Strontium, Barium, or Magnesium? H. J. HAMBURGER and C. L. ALONS (*Biochem. Zeitsch.*, 1919, **94**, 129—130).—The author has previously shown that dextrose may be retained by the frog's kidney perfused with a modified Ringer's solution (Hamburger and Brinkman, *Proc. K. Akad. Wetensch. Amsterdam*, September, 1917). When the perfusion fluid contains 0.06% of dextrose and the calcium is replaced by an equivalent amount of strontium or barium, the sugar is retained by the kidney, but such is not the case when an equivalent amount of magnesium is employed. If the solution is hypertonic with regard to dextrose, 0.1%, the same amount of sugar is found in the urine whether the perfusion fluid contains calcium, barium, or strontium. J. C. D.

The Formation of Phenol. MIDORI TSUBOI (*J. Biol. Chem.*, 1919, **38**, 13—16).—Phenol, but not cresol, is formed from tyrosine by the action of *Bacillus coli communis*. Phenol was not formed from phenylalanine. The significance of these observations with regard to the formation of phenols in the animal body is considered. J. C. D.

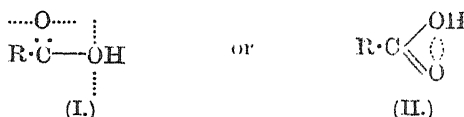
Bioluminescence. RAPHAEL DUBOIS (*Compt. rend. Soc. Biol.*, 1918, **81**, 484—485; from *Chem. Zentr.*, 1919, i, 241).—The investigations of Harvey (A., 1917, i, 365; 1918, i, 89) do not justify the replacement of the nomenclature "luciferase" by another name [compare Harvey, this vol., i, 299]. H. W.

The Relationship between Odour and Chemical Constitution. THOMAS H. DURRANS (*Perfumery and Essent. Oil Rec.*, 1919, **10**, 104—136).—The author gives a systematic survey of various classes of chemical compounds containing only carbon, hydrogen, and oxygen, or only two of these elements, and attempts to trace the cause of their odour or the lack of it, certain general conclusions being drawn for each class of compound. It is obvious that certain groups and linkings are sources of odour, but there are undoubtedly other powerful influences at work. Woker's theory that intramolecularly repelling forces increase the volatility of a compound, and consequently its odour, is partly correct, but breaks down with certain classes of ring compounds. A moderate molecular weight increases an odour, but a high molecular weight undoubtedly suppresses it. In certain circumstances, the closing of a ring does not affect the odour much, although in other not very different cases the effect is quite marked.

If the various osmophores, or sources of odour, are examined, it will be noticed that there is always a possibility of unsatisfied partial valencies or residual affinities existing, for example, the oxygen atom, the benzene ring, multiple linking, etc., all sources of odour and all possessing residual affinities. The author believes that such unsatisfied residual affinities are the prime cause of a chemical substance having an odour. If these affinities can be satisfied intramolecularly, no odour results. Thus the alcohols have unsatisfied residual affinities, the glycols have not; the alcohols have an odour, the glycols have not. It is necessary to assume that these



residual affinities can, under certain conditions, neutralise one another, and thus produce no odour, this neutralisation being influenced by the proximity of various groups. Thus with acids we may have



according as R is a light or a heavy group, substance I having an odour and substance II being odourless. On esterifying with an alcohol of low molecular weight, odour is again produced.

W. G.

Oxyhydrase, an Oxidising Reducing Ferment. Its Antitoxic Function. J. E. ABELOUS and J. ALOY (*Compt. rend. Soc. Biol.*, 1918, **81**, 783—785; from *Chem. Zentr.*, 1919, i, 383).—A ferment is present in milk as well as in other vegetable and animal secretions which can reduce nitrates and chlorates in the presence of an oxidisable substance (salicylaldehyde, anisaldehyde). The ferment decomposes water with the liberation of hydrogen and hydroxyl ions, and thus has reducing as well as oxidising power. Oxyhydrase is a factor in the antitoxic defence of the organism, and is adapted to the anaerobic life of the cells. H. W.

The Quantitative Excretion of Silicic Acid in Human Urine. M. GONNERMANN (*Biochem. Zeitsch.*, 1919, **94**, 163—173).—Normal human urine contains silica, the excretion of which may be raised by the ingestion of certain mineral waters. J. C. D.

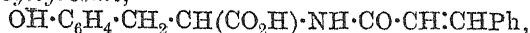
The Treatment of Wounds with the Carrel-Dakin Solution. K. OTTO (*Deut. med. Woch.*, 1917, **43**, 174—175; from *Chem. Zentr.*, 1919, i, 123).—The prescribed method of preparing the solution is too complicated for use in the field, and the following simpler process is recommended. Bleaching powder (200 grams) is

ground with water and addition of the latter is continued with constant stirring until the volume is 7 litres. A solution of sodium carbonate (140 grams) in water (2 litres) is added with stirring, and the solution is filtered. A solution of boric acid (40 grams) in water (1 litre) is added to the filtrate. Since this solution often causes a burning sensation it was later reduced to half strength and, in this form, rendered good service. Treatment with Dakin's solution has chiefly a prophylactic value.

H. W.

Behaviour of Cinnamic Acid and its Derivatives in the Animal Body. HIDEZO ANDO (*J. Biol. Chem.*, 1919, 38, 7—11).— α -Benzoylamino-cinnamic acid and *o*-benzoylamino-cinnamic acid were recovered from the urine unchanged after subcutaneous or oral administration to dogs or rabbits. Only small amounts of α -benzoylamino-*p*-hydroxycinnamic acid could be so recovered. Administrations of cinnamoyltyrosine by the mouth were followed by the appearance of hippuric acid in the urine. The substance is apparently broken down by the animal organism.

Cinnamoyltyrosine,



was obtained as its *ethyl* ester (m. p. 130°) by the action of sodium carbonate on mixed solutions of cinnamoyl chloride and tyrosine ester in chloroform. On hydrolysis with sodium hydroxide, cinnamoyltyrosine was obtained, crystallising in polygonal prisms, m. p. 166—167°.

J. C. D.

Metabolism of the Furan and Hydrofuran Derivatives in the Animal Body. NOBUYOSHI SUZUKI (*J. Biol. Chem.*, 1919, 38, 1—5).—Hydroxymethylpyromucic acid was isolated from the urine of rabbits which had received subcutaneous or oral administrations of chitose.

J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Absolute and Relative Disinfecting Power of Elements and Chemical Compounds. HANS FRIEDENTHAL (*Biochem. Zeitsch.*, 1919, 94, 47—68).—An exhaustive study of the disinfecting powers of a large number of products. The relative disinfecting powers of the elements in each group of the periodic classification are given, as well as information regarding many organic disinfectants. [See further, *J. Soc. Chem. Ind.*, 1919, July.]

J. C. D.

The Effects of Acids, Alkalis, and Sugars on the Growth and Formation of Indole by *Bacillus coli*. FRANK JOHN SADLER WYETH (*Biochem. J.*, 1919, 13, 10—24).—The activity of

B. coli in 2% peptone is determined by almost the same initial conditions of acid and alkaline reactions as is the case when fermentation is conducted in 2% dextrose peptone. The approximate limits of initial reaction are $p_H=4.27$ to 9.87 . A change of the initial reaction of the medium results in a change, similar in direction, but smaller in magnitude, in the final reaction of the culture. For *B. coli* grown in 2% dextrose peptone, whilst the initial reactions of the media vary from $p_H=4.30$ to 9.82 , the final reactions only vary between $p_H=4.27$ and 4.82 . When grown in 2% peptone the initial reaction may be from $p_H=4.30$ to 9.37 , and the final reaction from $p_H=5.92$ to 8.55 .

The proteolytic fermentation resulting in the peptone medium causes an increase of final alkalinity, unless the initial reaction lies between $p_H=9.37$ and 8.48 , in which case the final reaction is less alkaline than the initial reaction. The saccharolytic fermentation of *B. coli* in 2% dextrose peptone produces approximately constant amounts of acids and no appreciable amount of ammonia; on the other hand, when in a peptone medium the organism produces ammonia and acids in increasing amounts as the initial reaction of the medium increases in alkalinity. Formation of indole is retarded by the presence of free alkali or acid, whilst certain sugars also inhibit the formation of this substance by depressing the proteolytic activity of the bacillus.

J. C. D.

The Action of Electrolytes on the Electrical Conductivity of the Bacterial Cell and their Effect on the Rate of Migration of these Cells in an Electric Field. C. SHEARER (*Proc. Cambridge Phil. Soc.*, 1919, 19, 263—266).—A thick, creamy emulsion of the meningococcus or *B. coli* in neutral Ringer's solution (that is, one in which the sodium hydrogen carbonate is left out) has a resistance, as measured by electrical conductivity determinations, more than treble that of the same solution without the bacteria. If in place of Ringer's solution the emulsions are prepared with a solution of sodium chloride having the same conductivity as the Ringer's solution, a high resistance is obtained at first, but this rapidly drops, and at the end of thirty to forty minutes is the same as that of the saline solution alone. Further, it is found that immersion in such a solution for several hours kills the bacteria. If, when the resistance of such an emulsion in sodium chloride solution has dropped to normal, a little calcium chloride is added, the bacterial emulsion regains its high resistance and the bacteria are uninjured. Potassium, lithium, and magnesium chlorides act like sodium chloride, whilst barium and strontium chlorides act like calcium chloride. These results agree with those obtained by Loeb, Osterhout, and others with animal and plant cells.

The positive tervalent ions of lanthanum nitrate, and cerium and neo-ytterbium chloride and the negative tervalent ions of sodium citrate appear to have no action in increasing or decreasing the resistance of the bacterial cell as determined by the conductivity method, when used in very dilute solutions. On the other hand,

these salts and especially lanthanum nitrate, have a marked action in changing the rate of migration of these bacterial cells in an electric field. The addition of the lanthanum nitrate reduces the rate of migration, or, in other words, considerably alters the nature of the electrical charge on the bacterial cell wall. W. G.

Decomposition of Betaine by the Bacteria of "Guanol," a Fertiliser Prepared from Molasses Waste. ALFRED KOCH and ALICE OELSNER (*Biochem. Zeitsch.*, 1919, **94**, 139—162).—Organisms were found which attack betaine with the formation of trimethylamine, ammonia, and carbon dioxide. Methyl alcohol, formic acid, and acetic acid in small amounts appear to be the intermediate products in the production of carbon dioxide. [See further, *J. Soc. Chem. Ind.*, July, 1919.] J. C. D.

Action of Mixtures of Certain Salts on the Lactic Acid Fermentation. CHARLES RICHEL and HENRY CARDOT (*Compt. rend. Soc. Biol.*, 1918, **81**, 751—755; from *Chem. Zentr.*, 1919, **i**, 380).—The action of combinations of antiseptic salts on the lactic acid fermentation has been examined. Action is not additive; the more potent salt (copper sulphate) behaved after addition of cadmium sulphate as if the latter were not present. Addition of the sulphates of copper or zinc did not modify the antiseptic action of cadmium sulphate. H. W.

Fumaric Acid Fermentation of Sugar. C. WEHMER (*Ber.*, 1919, **52**, [B], 562—564).—A reply to Ehrlich (this vol., **i**, 239) denying that *Rhizopus nigricans* produces fumaric acid. J. C. W.

Influence of Varying Barometric Height on the Course of Alcoholic Fermentation and on Biological Processes in General. AUGUST RIPPEL (*Centr. Bakt. Par.*, 1917, [ii], **47**, 225—229; from *Chem. Zentr.*, 1919, **i**, 34).—The curves showing loss in weight due to the escape of carbon dioxide during slow fermentation show distinct zig-zags due to variations in the atmospheric pressure, the curve sinking with rising pressure and rising with decreasing pressure. The natural effect of change of pressure on the evolution of carbon dioxide must affect the course of fermentation in proportion as the yeast is influenced by the degree of saturation of carbon dioxide. The same considerations also apply to other biological processes in which a gas is evolved (ammonia, hydrogen sulphide, etc.), and a similar influence must also be operative in nature. H. W.

Ferment Action. IV. Further Studies on the Adsorption of Mixtures of Amino-acids with Polypeptides and Other Substances. Behaviour of Amino-acids and Polypeptides towards Albumin Solutions, Blood-Serum, and during the Coagulation of Sols. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, **2**, 211—224; from *Chem. Zentr.*, 1919, **i**, 95—96. Compare A., 1917, **i**, 306; 1919, **ii**, 49, 50).—The previous

observation that the presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and that conversely the adsorption of carbohydrates is adversely influenced by polypeptides, whilst in the presence of amino-acids the displacement of adsorption is one-sided, is confirmed by further examples. Thus the behaviour of proline is similar to that of other amino-acids, whilst glycine anhydride and pyrrolidonecarboxylic acid behave like dextrose. It is found that amino-acids and polypeptides can, in certain circumstances, be completely displaced by other amino-acids or higher polypeptides without the latter suffering displacement, but that the greater number only cause partial displacement.

The behaviour of various sols in this connexion has also been investigated with the possible aim of measuring the rate of adsorption and investigating its degree of dependence on the hydrogen-ion concentration of the solution. The sols investigated (ferric hydroxide, aluminium hydroxide, and arsenic sulphide) did not, however, adsorb amino-acids and polypeptides during coagulation. On the other hand, glycyl-*L*-leucine was adsorbed by coagulating blood serum.

H. W.

Ferment Action. V. Ultrafiltration Experiments with Mixtures of Amino-acids or Polypeptides with Yeast Juice. Evidence for the Colloidal Condition of Ferments and Extension of the Adsorption Theory. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1918, 2, 225—250; from *Chem. Zentr.*, 1919, i, 96. Compare preceding abstract).—The quantity of water employed in the maceration of yeast has great influence on the activity and stability of the juice. When ten times the amount of water is used, a stable juice, which is immediately active, is obtained; when three times the quantity of water is used, the initial activity of the juice is slight, but increases rapidly on keeping, and finally reaches a maximum which is never attained in the former case. Difference appears to depend on an alteration in the state of the ferment, for example, its dispersivity with dilution. In this connexion, a series of ultra-filtration experiments have been performed. The extracts, obtained from various dried yeasts, had very differing activities towards glycyl-*L*-leucine. Yeast juices mixed with the latter or with *γ*-leucine yielded filtrates which were always poorer in amino-nitrogen than the original mixtures, the loss being relatively greater from dilute than from concentrated solution. The originally inactive yeast juices also had power of adsorption, and the equilibrium is independent of the amount of hydroxyl ions present. Adsorption occurs with polypeptides (glycyl-*D*-leucine) which are not attacked by yeast juice. Under equivalent conditions, the adsorption of a complex polypeptide is greater than that of a dipeptide. With decrease in the fermentive activity of a juice by age or by heat a decrease in adsorptive capacity is observed which may sink to zero. Considered in connection with the observation that adsorption can occur with inactive juices, this leads to the deduc-

tion that whilst adsorption of the substrate by the colloidal ferment precedes fission, the latter process does not necessarily follow the former. Further evidence is shown by the behaviour of glycyl-L-leucine, which, at 0°, is adsorbed by yeast extract, but not decomposed.

The temperature-coefficient of fission of polypeptides generally lies between 1.3 and 2.4 according to conditions (yeast extract, temperature, hydrogen-ion concentration, and substrate). The optimum temperature for $p_H=7.50$ is between 50° and 55°.

The chief results of the work in this field are collected and reviewed.

H. W.

The Nitrogenous Constituents of Yeast. JAKOB MEISENHEIMER (*Zeitsch. physiol. Chem.*, 1919, 104, 229—283).—An investigation of the nature of the monoamino-acids present in the products of autolysis derived from bottom and top fermenting yeasts. The estimations were carried out by the ester method of Fischer. Glycine, alanine, valine, leucine, proline, phenylalanine, aspartic and glutamic acids, tyrosine, and tryptophan were identified. Serine and cystine were recognised with less certainty, and there was also evidence of the presence of an aminobutyric acid. Glucosamine was isolated from the cell residue of the autolysis.

J. C. D.

Enzymatic Power of Yeast. TH. BOKORNY (*Allgem. Brau.-Hopf. Zeit.*, 1918, 58, 1093—1094; from *Chem. Zentr.*, 1919, i, 96—97).—Experiments are described on the inhibiting action of disinfecting agents, even in minute quantity, on the fermentative activity and other enzymatic powers of yeast. Formaldehyde (0.2%) retards growth and fermentation, the yeast is killed, as is also the fermentation ferment; 0.05% does not destroy the activity of the latter. 0.1% Kills zymase within two days, but 1% does not render invertase inactive in the same time, sugar solution being strongly inverted. It is therefore possible with the aid of formaldehyde to prepare a yeast which can invert, but not ferment, sugar. Phenylhydrazine (0.5%) inhibits the fermentation of maltose, but not of dextrose. Fermentation persists slightly in the presence of mercuric chloride (0.02%), but is inhibited by 0.1%, although sucrose is still powerfully inverted. The action of silver nitrate is similar. Alcohol (10%) does not cause a permanent inactivity of zymase within five days, and, even after twenty days, slight fermentative power persists. Absolute alcohols destroy the power to ferment within ten minutes.

H. W.

Alterations in the Metabolism and Cellular Permeability at Temperatures near the Freezing Point. E. PANTANELLI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 205—209).—When cooled to a temperature closely approaching the freezing point, the endocarp cells of the almond exhibit a progressive increase of the cellular permeability, which is rendered evident by rapid emission of water from the tissue in a dry atmosphere and by exosmosis of substances

from the tissue immersed in water. This phenomenon is accelerated by the presence of certain compounds which penetrate rapidly into the cell, such as glycerol, ethyl alcohol, citric acid, and free alkali. Such increase in cellular permeability is accompanied by rapid destruction of the sugars; this effect may be restricted by supplying either substances capable of being absorbed and utilised for the respiration, for instance, glycerol, ethyl alcohol, or citric acid, or substances which retard the exosmosis of the sugars, or intermediate products of the respiration, such as sodium chloride, potassium phosphate, and citric acid. Sugars (sucrose, dextrose) present in the external liquid do not exert a similar restricting action, since they are not absorbed. A further phenomenon caused by the low temperature is intense auto-digestion of the proteins, this being enhanced by exosmosis of the soluble products of the digestion and by rapid destruction of the sugars. T. H. P.

Influence of Fluorides on Vegetation. A Preliminary Experiment in Flower Pots. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, 168, 976—982).—As the result of pot trials, using wood charcoal to which the necessary nutrients had been added as a culture medium, the authors find that fluorine in the form of potassium fluoride exerted a favourable influence on the growth of seven species of plants, had no effect on three, and caused a lower crop yield in the case of three. W. G.

Comparative Rate of Absorption of Various Salts by Plant Tissue [Carrot and Potato]. WALTER STILES and FRANKLIN KIDD (*Proc. Roy. Soc.*, 1919, [B], 90, 487—504).—The rate of absorption of various chlorides, sulphates, nitrates, and potassium salts from solutions of 0.02*N*-concentration was measured by the electrical conductivity method. A rapid withdrawal of salt from solution occurred during the first few hours, after which the absorption proceeded to an equilibrium over a period of several days, the curve being approximately logarithmic in the latter case. Cations were absorbed in the orders K, Ca or Na, Li, Mg or Zn, Al, and K, Na, Li, Ca, or Mg, and anions in the orders SO₄, NO₃, Cl, and NO₃, Cl, SO₄, during the initial and equilibrium periods respectively, these results being generally in agreement with those obtained by Ruhland, Fitting, Pantanelli, and Troendle, who failed to differentiate between the initial and equilibrium stages. The rate and extent of intake of one ion of a salt were found to be influenced by the nature of the other ion, and, as previously observed by Rothert and Meurier in the case of aluminium sulphate, aluminium was absorbed much more rapidly than its anion. According to Troendle, the rate of absorption of the metallic ions in any group of the periodic classification increases with the atomic weight. It is pointed out that although this view is not contradicted by the present results, the latter show equally that the initial rate of absorption is largely dependent on the mobility of the ions or diffusibility of the salt, and that the

position of equilibrium appears to be governed by some quite different property, since at this stage the bivalent ions, Ca, Mg, SO_4 , are absorbed to a much smaller extent than the univalent ions, K, Na, Cl, NO_3 . W. E. F. P.

Fatty Oil from the Seeds of the Evening Primrose [*Oenothera biennis*], and a New Linolenic Acid. A.

HEIDUSCHKA and K. LÜFT (*Arch. Pharm.*, 1919, 257, 33—69).—The air-dried seeds of the evening primrose contain water (13.95%), crude proteins (13.38%), fat (16.93%), fibre (14.56%), nitrogen-free extractives (35.03%), and ash (6.15%). The oil was obtained by extraction of the crushed seeds with ether, and formed a golden-yellow substance resembling poppy oil in taste and odour; it remained completely liquid at 0° , but a few solid particles separated at -11° . It had $D_{20}^{25} 0.9283$, $n_D^{20} 1.4722$, acid number 0, saponification number 195.2, Reichert-Meissel number 2.61, Polenski number 0.57, iodine number 148.92, Hehner number 94.94, acetyl number 13.9. It was optically inactive and a member of the class of drying oils. The volatile fatty acids consisted mainly of hexoic acid (0.81%). Separation of the unsaturated and saturated fatty acids was effected in the usual manner by means of the lead salts, and the former were brominated in glacial acetic acid-etheral solution. Under these conditions, a sparingly soluble *hexabromo- γ -linolenic acid*, microscopic needles, m. p. $195-196^\circ$ (decomp.), separated which, when treated with zinc and alcohol, yielded *γ -linolenic acid* as a yellow substance of unpleasant odour. Tetrabromo- α -linoleic acid, tetrabromo- β -linoleic acid, and dibromo-oleic acid were identified in the filtrates from hexabromo- γ -linolenic acid. The unsaturated fatty acids contain *γ -linolenic acid* (2.50%), *α -linoleic acid* (30.20%), *β -linoleic acid* (38.11%), and *oleic acid* (29.19%). Oxidation of the unsaturated fatty acids with permanganate yielded dihydroxystearic acid, a mixture of tetrahydroxystearic acids, and *γ -hexahydroxystearic acid*, minute needles, m. p. 245° (decomp.).

Fractionation of the saturated fatty acids from alcohol or by means of their magnesium salts led to the isolation of palmitic acid and a substance the properties of which agree with those of daturic acid; theoretical considerations caused the authors to doubt the natural occurrence of the latter acid, and experiments on the fractional distillation of the substance with steam showed that the "daturic acid" obtained from the evening primrose, at any rate, was a mixture of palmitic acid (and possibly stearic acid) with acids of greater molecular weight.

The unsaponifiable matter of the oil contained phytosterol (2.27%), the acetate of which had m. p. 130.3° (corr.). H. W.

Investigations on the Anthocyanin Metabolism on the Basis of the Chemical Properties of the Anthocyanin Group.

K. NOACK (*Zeitsch. Bot.*, 1918, 10, 561—628; from *Physiol. Abstr.*, 1919, 4, 99).—A study of *Polygonum compactum* and various

Paeonia species and varieties. In the first days, leaves of *Polygonum compactum* have an intense red coloration, which fades away in the following days, and the leaves finally become green. The following explanation of this phenomenon is suggested. Anthocyanin is dissociated by means of an enzyme into anthocyanidin and sugar. The anthocyanidin is isomerised into a colourless pseudo-base, and this, during its oxidation, can become transformed into a yellow pigment which, by photochemical reduction, may again give the pseudo-base of anthocyanidin. The amounts of anthocyanidin and its oxidation product vary inversely with one another. The variations are influenced by light, since the pseudo-base is formed by photochemical reduction of the oxidation product of the pigment. In the dark, anthocyanidin is again oxidised, this process being accelerated by heat, light and temperature thus having an antagonistic action. An oxidation product of anthocyanidin, but not anthocyanidin itself, is found in the vegetative organs of various *Paeonia*, and the amount of this oxidation product varies directly with the amount of anthocyanin in the plant. In the flowers, in addition to the oxidation product, the anthocyanidin pseudo-base may occur, but only in small quantities, and without any relation to the amount of anthocyanin formed in the development of the flower.

W. G.

Occurrence of Vanillin. EDMUND O. VON LIPPMANN (*Ber.*, 1919, 52, [B], 905).—The occasional presence of vanillin in potato tubers, particularly in the layers immediately beneath the skin, has been frequently observed. It is now found that vanillin can also be extracted from the fresh, blue blossoms (but not from the white ones); it disappears fairly rapidly from the plucked flowers.

H. W.

Preparation of Sucrose from Plants. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 104, 217—219).—The ether extracted fruits of *Sapindus utilis* were extracted with boiling alcohol in the presence of potassium carbonate. The filtered extract, after concentration, was treated with freshly precipitated lead hydroxide for six days. From the lead-free filtrate, a fraction was obtained by extraction with methyl alcohol, which gave sucrose on crystallisation.

J. C. D.

The Protein Extract of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, 41, 670—682. Compare A., 1917, i, 618).—Three large samples of ragweed pollen have been percolated with ether and 95% alcohol (loss in weight, about 22%), and the residue examined for proteins by repeated macerations with (a) water, (b) 10% salt solution, (c) 0.2% potassium hydroxide. The aqueous extract was found to contain an albumin (1.2%), coagulating at about 45—50°, and proteoses (3%), and when partly saturated with ammonium sulphate gave a precipitate consisting of albumin and proteose in the proportion 3:1, and causing

anaphylaxis in guinea-pigs. After precipitating all the protein from this extract by means of ammonium sulphate, and then removing the sulphate, phosphotungstic acid gave a precipitate of the following bases: adenine, guanosine (?), histidine, arginine, lysine, and agmatine, these being identified by the usual methods. The 10% salt extract gave a small amount of the above albumin and but very little evidence of the presence of a globulin. The dilute alkali extract contained the chief protein, which is therefore a glutelin, amounting to about 2.9% of the weight of the pollen, and appearing as an almost white, dusty powder. J. C. W.

A Proximate Analysis of *Rumex crispus*, and a Comparison of its Hydroxymethylantraquinones with those from Certain Other Drugs. GEORGE D. BEAL and RUTH E. OKEY (*J. Amer. Chem. Soc.*, 1919, 41, 693—706).—An examination of the extract made by percolating the dried and powdered root of the common yellow (curled) dock with cold 95% alcohol. The constituents which are soluble in water, yielded small quantities of emodin, a mixture of emodin monomethyl ether and chrysophanic acid, dextrose and a little lævulose, and organic acids and much resinous material. The insoluble portion of the extract contained emodin, its monomethyl ether, chrysophanic acid, a phytosterol, palmitic, stearic, and erucic acids with lower unsaturated and higher saturated fatty acids, a small amount of a hydrocarbon, an essential oil, some glucosides, and much resin.

A cursory examination of cascara and aloes has also been made, mainly with the aim of isolating their emodins. *Rumex* emodin is identical with that of cascara (Jowett, A., 1905, ii, 192) and isomeric with the aloes-emodin of aloes and senna. The phytosterol is also the same as the "rhamnol" of cascara.

The yield of emodin from the dried dock root is about 0.1%, and that of chrysophanic acid somewhat less. This compares favourably with the quantities obtainable from more expensive drugs.

J. C. W.

Toxicity of "Alkali" Salts. THAKUR MAHADEO SINGH (*Soil Sci.*, 1918, 6. 463—477).—An examination of the effect of various sodium salts on ammonifying, nitrifying, and nitrogen-fixing organisms, and on the germination and growth of wheat and peas. Arranged in order of descending toxicity, the salts examined are sodium chloride, nitrate, carbonate, and sulphate, the percentage of the anion, and not of the cation, being the determining factor. Small amounts of each of the different salts used stimulated both crop growth and bacterial activity, the amount varying with the crop grown. The toxicity point as found when salts were used in combination, as under field conditions, agreed very closely with the points found when the individual salts were used. The toxic point of the combined salts depended on the percentages of the chlorides, nitrates, carbonates, and sulphates present, and the combination in which they existed. Calcium sulphate when present

lowered the toxic point of the chloride, carbonate, or nitrate of sodium. W. G.

Alfalfa [Lucerne] Investigation. VII. Alfalfa Saponin. C. A. JACOBSEN (*J. Amer. Chem. Soc.*, 1919, 41, 640—648).—When alfalfa hay is extracted with hot alcohol and the solution is cooled, a voluminous, green precipitate is deposited, from which ether extracts two ketones, myristone and alfalfone (A., 1912, ii, 80; i, 239). The insoluble, gummy residue left in the Soxhlet thimble contains a saponin, which may be isolated by dialysis of the aqueous solution and reprecipitation with alcohol. Alfalfa [lucerne] saponin, $C_{27}H_{37}O_{16}N$, is a brown, amorphous powder, decomp. 280—300°, readily soluble only in water and glycerol, and may be hydrolysed to a sapogenin, $C_{18}H_{18}O_{10}N$, dextrose, and a pentose. It also forms an acetyl derivative, but this may be the acetate of the sapogenin. Its solution has an enormous surface tension, minute quantities producing a remarkable foam in aerated beverages, and bubbles 4 inches in diameter being possible with a 25% solution.

The saponin differs from most compounds of this type in containing nitrogen. It is also abnormal in that it does not hæmolyse blood. It is toxic to fish, but this generally accepted property of saponins as a class seems to be due to their power of preventing the diffusion of air into the water, for the golden carp, which has the instinct to rise to the surface to breathe, will live in saponin solutions (1 to 35,000), whereas the black bass succumbs. Alfalfa saponin causes acute local irritation and death when injected subcutaneously, but is harmless when taken *per os*.

The crude saponin is accompanied by a yellow substance, "saponin X," and alfalfa also contains two proteins and a bitter principle, which are being investigated. J. C. W.

Effect of Manganese on the Growth of Wheat. A Source of Manganese for Agricultural Purposes. J. S. McHARGUE (*J. Ind. Eng. Chem.*, 1919, 11, 332—335).—Results of pot cultures showed that the addition of manganese increases the size and nitrogen content of wheat grains, and stimulates the growth of the plant; the most favourable quantity appeared to be about 0.028% of manganese, calculated on the total weight of the soil in the pot. It was added in the form of manganese carbonate. Basic slag contains an average of 4.8% of manganese, and it is possible that some of the benefit to crops resulting from the use of this fertiliser is due to the presence of manganese. W. P. S.

Solubility of the Calcium, Magnesium, and Potassium in such Minerals as Epidote, Chrysolite, and Muscovite, especially in regard to Soil Relationships. R. F. GARDINER (*J. Agric. Res.*, 1919, 16, 259—261).—When the finely powdered minerals were left in contact with the aqueous extract from an acid soil for two months at 25°, it was found that 1.6% of the total calcium in the epidote, 0.21% of the magnesium in the

chrysolite, and from 11 to 21% of the potassium in the muscovite was extracted under the experimental conditions. W. G.

Decomposition of Cyanamide and Dicyanodiamide in the Soil. G. A. COWIE (*J. Agric. Sci.*, 1919, 9, 113—136).—Experiments on field plots and on soil in pots show cyanamide to be decomposed in soil, yielding ammonia, which is then nitrified in the usual way. The conversion of the nitrogen of the cyanamide into nitrate is almost quantitative. Dicyanodiamide undergoes no decomposition. On adding both substances together to soil, it is found that the dicyanodiamide does not prevent the formation of ammonia from the cyanamide, but that it largely prevents nitrification. In a mixture of the two substances containing 25% of dicyanodiamide, only 22% of the nitrogen is converted into nitrate, and in a mixture containing 75% of dicyanodiamide, only 5%. Dicyanodiamide is thus toxic to the nitrifying organisms. On the ammonifying bacteria it has no effect, as dried blood readily undergoes ammonification in its presence, and the ammonia produced accumulates in the soil owing to the action of the nitrifying organisms being prevented. These results show that cyanamide is not normally converted into dicyanodiamide in soil; they also suggest the possibility of a di-imino-formula for dicyanodiamide. [See also *J. Soc. Chem. Ind.*, 1919, 380A.] J. H. J.

Soluble Non-protein Nitrogen of Soil. R. S. SNYDER and R. S. POTTER (*Soil Sci.*, 1918, 6, 441—448).—From a further study of the method previously described (A., 1917, i, 75), the authors find that, in order to obtain the maximum soluble non-protein nitrogen from basic soils, they should be extracted with 1% hydrochloric acid until the washings show no calcium. It is unnecessary to extract acid soils with the acid. Nitrates in the acid extract may be reduced by Devarda's alloy after making the extract faintly alkaline. The examination of a number of soils shows that the amount of the unknown soluble non-protein nitrogen is usually decreased by an application of lime, although there are exceptions. W. G.

Manuring Experiments with "Kalikalk." H. G. SÖDERBAUM (*Medd. No. 163, Centralanstalten försöks. jordbruk; from Bied. Zentr.*, 1919, 48, 135—136).—This preparation (prepared by heating together potash felspar, limestone, and gypsum at 1150°) gave good results in the manuring of oat crops. [See further, *J. Soc. Chem. Ind.*, 1919, July.] J. C. D.

Organic Nutrients for Green Plants. TH. BOKORNY (*Biochem. Zeitsch.*, 1919, 94, 78—83).—Sulphite lye from the cellulose industries, even after the removal of the majority of the sugar, is of considerable value as a manure. The value of human urine, as a nutrient for plants is also great. The presence of hippuric acid in the urine of certain domestic animals makes this waste product less useful than human urine. This may be due to the toxic influence of the benzoic acid. J. C. D.

Organic Chemistry.

The Atom Model of Rutherford and Bohr in Chemistry.

A. E. LACOMBLÉ (*Chem. Weekblad*, 1919, 16, 832—834).—A discussion of various difficulties which arise in the further development of the ideas suggested by Buchner (this vol., i, 245) in his application of the Rutherford-Bohr theories of atomic structure to the case of atom linking in organic compounds. If the single bond between two carbon atoms be constituted by the attraction of two valency electrons revolving in an orbit perpendicular to the line joining the two positive nuclei, then, in addition to the electrostatic field, an electromagnetic field is established the direction of which is determined by the sense of the motion of the electrons in the orbit. In the case of the methane molecule there would thus be several possible isomerides owing to the possibility of positive or negative rotation of the electrons in the four atomic bonds as viewed from the carbon nucleus. Two of these isomerides are symmetrical, the rotations in one being all positive and in the other all negative. These are enantiomorphous isomerides, and each gives rise to one derivative of the formula CH_3R and one CH_3R_2 . The unsymmetrical possibilities may be represented as $+++-$, $+-+-$, $----$. Each of these gives two isomeric mono-derivatives of the formula CH_3R . As these are unknown, it may be assumed that only the symmetrical forms exist. In chains of carbon atoms "positive" carbon atoms must alternate with "negative" atoms, so that a closed ring is only possible with an even number of atoms, unless for the odd atom an abnormal structure is assumed, which would again render possible the existence of unknown isomerides. It is also pointed out that the displacement of the electrons to form orbits between the carbon atoms of the diamond would probably be indicated in the Röntgen diagram of the crystal by the presence of lines. Such lines have not been observed. W. S. M.

The Nature of the Ethylenic and Acetylenic Linkings in Carbon Compounds. W. E. GARNER (*Chem. News*, 1919, 119, 16—17).—The appearance or disappearance of the unsaturated linking in carbon compounds is generally accompanied by *trans*-elimination or *trans*-addition of the groups leaving or entering the molecule. An explanation of the mechanism of such reactions is offered in terms of Bohr's theory of the arrangement of the atoms and electrons in the molecule. It is shown by means of diagrams that when two univalent atoms, for example, hydrogen and bromine, become detached from two adjacent carbon atoms, with formation of an ethylenic linking, this is more likely to occur in the *trans*- than in the *cis*-position. E. H. R.

New Practical Method of Carbonising Coal at Low Temperatures. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919, 52, [B], 1035—1039).—Difficulties are encountered in carbonising

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considerable quantities of coal at low temperatures in a reasonable time since, owing to the low thermal conductivity of the material, the heat penetrates so slowly into the interior of the charge that the outer portions readily become overheated. The authors consider that the conditions essential for success are that the volatile portions should not be heated to a temperature higher than that necessary for their volatilisation and that they should not be exposed to this temperature for an unnecessarily long period. They have therefore constructed a cylindrical retort which can be rotated round a horizontal axis. The latter is hollow, but is plugged in the middle. Through the one end steam is admitted which carries off the volatile products through the other end to a suitable condensing arrangement. The furnace is heated from underneath by a series of gas burners fed with air under pressure, whilst loss of heat is prevented by enclosing the furnace with a metal sheath. A thermo-couple is placed in the axis. The furnace permits the distillation of 20 kilos. of coal in one to two hours. Distillation generally commences at about 350° and is complete at 500° . The yield of tar is 3—30%, according to the kind of coal used. The first portions of the oils are lighter than water, the last portions are heavier, the mean density being slightly greater than unity. The tar appears in thin layers as a golden-red oil, which is more or less viscous according to the kind of coal used. H. W.

Paraffin from Coal. W. GLUUD (*Ber.*, 1919, 52, [B], 1039—1053).—The occurrence of paraffin in low-temperature tars has been frequently noted, but little is known as to the nature of the individual components. The author has therefore investigated the tar derived from a Mond gas plant fed with a gas coal and finds the paraffin to be a mixture of saturated normal paraffins terminating with $C_{29}H_{60}$, in which hexa- and hepta-cosane preponderate. The series thus appears to be less comprehensive than with brown coal paraffins.

[With FR. HENNY HÖVERMANN.]—The paraffin exists as such in the crystalline state in the tar, from which it is isolated by treatment of the latter with acetone; in the earlier experiments attempts were made to isolate a pure product by repeated crystallisation of the crude substance, first from acetone and subsequently from benzene. In this manner, heptacosane was ultimately isolated. Better results, however, were obtained by repeated fractional distillation of the crude product under diminished pressure and crystallisation of the individual fractions when necessary. The complete series from $C_{24}H_{50}$ to $C_{29}H_{60}$ could thus be isolated, the identity of the products being established by direct comparison with the synthetic substances. Heptacosane was prepared by the action of phosphorus pentachloride on myristone and treatment of the chloride with hydriodic acid; contrary to the usual assumption, however, the intermediate product was found to be *xxx-trichloro-n-heptacosane*, needles, m. p. about 30° , the formation of which is attributed to the ketone reacting in its enolic form and addition of

chlorine occurring at a higher temperature. Octacosane was prepared in satisfactory yield by the electrolysis of a mixture of myristic and palmitic acids. The following constants are recorded for the synthetic hydrocarbons: $C_{26}H_{54}$, n_D^{25} 1.43332, n_D^{25} 1.43096, n_F^{65} 1.43851, n_D^{80} 1.42774, n_C^{80} 1.42534, n_F^{80} 1.43293; $C_{27}H_{56}$, n_D^{25} 1.43453, n_C^{65} 1.43228, n_F^{65} 1.43992, n_D^{80} 1.42874, n_C^{80} 1.42636, n_F^{80} 1.43411; $C_{28}H_{58}$, n_D^{25} 1.43539, n_C^{65} 1.43309, n_F^{65} 1.44071, n_D^{80} 1.42971, n_C^{80} 1.42737, n_F^{80} 1.43501.

Investigation of the paraffins obtained from other varieties of coal rendered it very probable that they are closely similar in composition. The isolation of small amounts of paraffin by the direct extraction of coal with benzene at 260–270° leads the author to the conclusion that it exists in all probability to some extent as such in coal, and is therefore not exclusively a product of secondary processes occurring during distillation. H. W.

Light Petroleum from Coal. FRANZ FISCHER and W. GLUUD (*Ber.*, 1919, 52, [B], 1053–1068).—The object of the investigation was to get a general insight into the nature of the most volatile fractions of low-temperature tar. It was found that considerable quantities (about 1% of the weight of the coal) of light petroleum could be obtained, and that benzene is not present in more than minimal amount.

Three different coals were investigated, a gas coal (Zecke Lohberg) and two fat coals (Flöz Albert and Minden). The latter was of interest, since the mine from which it was obtained was known to smell of petroleum; the coal evolved paraffins at a temperature well below that at which carbonisation commenced, so that it is established that light paraffins can exist pre-formed in certain coals. The light petroleum was isolated from the gas and also from the tar. In the former case, since it was desired to operate in a technical manner, extreme cooling as with liquid air was not adopted; the products were isolated either by liquefaction by compression in steel cylinders or, preferably, by compression into paraffin oil and isolation from the latter by treatment with steam. In this manner the considerable fraction boiling below 20° was lost; the product had b. p. 20–100° with only small portions of higher boiling point. The tar was treated with steam and the distillation was discontinued when only small quantities of oil came over, since otherwise considerable quantities of phenolic substances distilled. The boiling point of the distillate was mainly 60–200°. All the fractions contained sulphur compounds. They were purified by treatment with alkali and then with concentrated and 15% fuming sulphuric acid or, preferably, with aluminium chloride; the use of liquid sulphur dioxide proved less advantageous. Perfectly colourless liquids were thus obtained, which were stable towards light and air. The fraction, b. p. 20–60°, was composed of saturated paraffin hydrocarbons; that of b. p. 60–100° contained naphthenes mixed in the case of the gas coal with paraffins. The composition of the higher fractions, b. p.'s 100–125° and 125–190°, was less definite; they

appeared to be mixtures of paraffins with naphthenes with higher hydrogen content and, probably, complex aromatic compounds.

The fractions, b. p. 60—100°, were examined for benzene; the presence of the latter in small amount was established in a product obtained from the Minden coal and purified with liquid sulphur dioxide, the isolation being directly effected by exposure to low temperature, but the quantity present cannot exceed 3%. The fractions obtained from the second fat coal and from gas coal and purified by aluminium chloride appeared to be free from benzene when examined by the triphenylmethane method. The usual identification by successive conversion into nitrobenzene and aniline appeared inadmissible in this instance owing to the danger of the formation of benzene by the oxidation of more highly hydrogenated products.

The behaviour of the several fractions when cooled has also been fully investigated; the original paper must be consulted for details.

H. W.

Preparation of some Volatile, Saturated Acyclic or Cyclic Hydrocarbons contained in Light Petroleums.

G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **168**, 1324—1326).—A number of aliphatic and cyclic hydrocarbons have been prepared and their b. p.'s, densities, and critical temperature of solution in aniline determined. The following results were obtained:

	Crit. temp. sol. in aniline.	B. p.	Density.
Pentane	72.0°	36.3°	D ₀ ^d 0.6454
isoPentane	77.0	28.0	D ₀ ^d 0.6394
isoHexane.....	73.8	61.7—62.4	D ₁₅ ^d 0.658
isoHeptane	72.8	90—91	D ₁₅ ^d 0.6842
Heptane... ..	70.0	98—98.3	D ₁₅ ^d 0.6879
Octane.....	71.8	125.8	D ₁₅ ^d 0.7063
Methylcyclohexane	41.0	100.4	D ₀ ^d 0.780
1:2-Dimethylcyclohexane ...	42.1	128.6—129	D ₁₅ ^d 0.798
1:3-Dimethylcyclohexane ...	49.7	121.2—121.8	D ₁₅ ^d 0.775
1:4-Dimethylcyclohexane ...	48.0	122.7—123	D ₁₅ ^d 0.783
cyclopentane	18.0	49.5	D ₁₅ ^d 0.750
Methylcyclopentane.....	35.0	72.0	D ₁₅ ^d 0.753

The authors find that, for the conversion of butyric, adipic, or methyladipic acid into its corresponding ketone, manganous carbonate is a very effective catalyst.

W. G.

Decomposition of Acetylene at High Temperatures in the Presence of Various Catalysts.

SIEGFRIED HILPERT (*Ges. Abhand. Kennt. Kohle*, 1917, **1**, 271—275; from *Chem. Zentr.*, 1919, **i**, 709—710).—Experiments were undertaken with the object of polymerising acetylene to benzene, but a relatively satisfactory yield of the latter could not be obtained. In all cases, primary decomposition appears to involve the separation of carbon, and the formation of tar or benzene appears to be a secondary change. The acetylene was prepared from calcium carbide and purified by

passage over a long layer of kieselguhr impregnated with a solution of cuprous chloride in hydrochloric acid. The furnace consisted of an electrically heated Jena-glass tube. With coke as catalyst, it was found that the impurities in the material, particularly sulphur, took part in the change. With glass splinters, a fog of tar appeared at 400°, whilst at 500° a layer of carbon was slowly formed on the glass and a mixture of benzene and tar containing unsaturated substances was obtained; the decomposition of acetylene on glass appeared to be characterised by the formation of carbon at a relatively high temperature and the simultaneous production of tar. With powdered iron and more markedly with nickel, decomposition commenced at 300° and proceeded so rapidly at 400° that the tube rapidly became choked with carbon; the tar was strongly unsaturated and contained but little benzene. Aluminium, mercury, lead, zinc, and tungsten had little action. With copper a brown deposit rapidly formed, which soon choked the tube completely, whilst an unpleasant smelling tar was formed in small amount. Brass filings, on the other hand, only became slowly coated with carbon and gave a tar similar to that obtained with glass. Molten phenanthrene or anthracene did not react with acetylene in the presence or absence of aluminium chloride.

H. W.

The Interaction of Acetylene and Mercuric Chloride.

DAVID LEONARD CHAPMAN and WILLIAM JOB JENKINS (T., 1919, 115, 847—849).

Action of Methyl Sulphate on the Alkali and Alkali-earth Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 168, 1204—1206. Compare this vol., i, 308).—The alkali and alkali earth sulphates if heated with methyl sulphate in sealed tubes at varying temperatures yield the pyrosulphate of the metal and dimethyl ether. This is shown to be due to the direct interaction of the two sulphates, and not to the intermediate formation of a sulphate such as sodium methyl sulphate, which would subsequently break down to the pyrosulphate and methyl ether. W. G.

The Hydrolysis of Ethyl Sulphite. A. BAGGESGAARD-RASMUSSEN (*Ber.*, 1919, 52, [B], 1069—1078).—The work of previous investigators has shown definitely that ethanesulphonate is formed in small amount during the hydrolysis of ethyl sulphite by alkali hydroxide, but an explanation of the phenomenon has not been given. The author has performed a series of quantitative experiments under different conditions, and has measured both the amount of base unused and the quantity of sulphite formed; the extent of hydrolysis as indicated by the first method is invariably slightly greater than that shown by the second, but a part of the difference is to be ascribed to an unavoidable slight oxidation of the sulphite. The actual formation of sodium ethanesulphonate is, however, placed beyond doubt. The author finds that the hydrolysis of ethyl sulphite by bases is in the main an absolutely

normal process; if, however, the action occurs slowly (as with the equivalent amount of alkali), small quantities (about 4—5%) of ethanesulphonate are produced. This compound is shown to be formed by the action of ethyl sulphite on the alkali sulphite first produced.

H. W.

Biochemical Formation of Mercaptans. F. F. NORD (*Ber.*, 1919, 52, [B], 1207—1211).—Neuberg and Nord (A., 1914, i, 1046) have shown that thioacetaldehyde is reduced to ethyl mercaptan by living yeast and also by zymase solution. The present investigation deals with the possibility of a similar process occurring with higher thioaldehydes. For biochemical purposes, it is unnecessary to isolate the difficultly accessible thioaldehydes in a state of purity; it is sufficient to treat the aldehydes with an alcoholic solution of ammonia and hydrogen sulphide, when homologues of thialdine are produced which behave as if they were mixtures of thioaldehyde and aldehydeimine, and possess the further advantage of being freely soluble in aqueous alcohol. *n*-Butaldehyde was treated in this manner and the product added to a solution of sugar in water which was undergoing brisk fermentation by yeast. Hydrogen sulphide was freely evolved, and, after fermentation had ceased, the liquor was found to contain *n*-butyl mercaptan, b. p. 95—102°, in small amount, together with indefinite compounds of higher boiling point. The presence of acetaldehyde was also established. In a similar manner, *iso*amyl mercaptan, b. p. 115—119°, was obtained from *isovaleraldehyde*; the thiovaleridine had a marked inhibitive action on the fermentation.

H. W.

Interaction of Mercuric and Cupric Chlorides Respectively and the Mercaptans and Potential Mercaptans. PRAFULLA CHANDRA RÂY (T., 1919, 115, 871—878).

Water of Crystallisation: Compounds with $2\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$. I. GUARESCHI (*Gazzetta*, 1919, 49, i, 134—140. Compare A., 1915, ii, 774).—Strontium formate loses its $2\text{H}_2\text{O}$ either (1) at 30°, or (2) at the ordinary temperature and a pressure of 20 mm. and in presence of sulphuric acid, the last $\frac{1}{2}\text{H}_2\text{O}$ being given up only very slowly; the anhydrous salt does not recover the water of crystallisation in the air. Zinc formate ($+2\text{H}_2\text{O}$) loses its water at 70° (not at 60°), the anhydrous salt reabsorbing about $1\frac{1}{2}\text{H}_2\text{O}$ from the air. Manganese formate loses its $2\text{H}_2\text{O}$ only at 70°, the last $\frac{1}{2}\text{H}_2\text{O}$ very gradually. Calcium chlorate ($+2\text{H}_2\text{O}$) undergoes complete dehydration at 50°, the anhydrous salt recovering all its water and then deliquescing in the air. Potassium ferrocyanide ($+3\text{H}_2\text{O}$) loses its water of crystallisation entirely either (1) at 50°, or (2) at 42° in a current of air, or (3) at the ordinary temperature in a desiccator over calcium chloride; in all cases, the last $\frac{1}{2}\text{H}_2\text{O}$ is released extremely slowly.

From the observation that many salts appear to yield their water

of crystallisation in definite fractions, the conclusion is drawn that the true molecular weights for the hydrated salts are multiples of those corresponding with the simplest empirical formulæ.

T. H. P.

The Solubility of Silver Acetate in Acetic Acid and of Silver Propionate in Propionic Acid. JOSEPH KNOX and HELEN REID WILL (T., 1919, 115, 853—854).

Stearic and Palmitic Esters of the Isomeric Propylene Glycols. L. ISABEL HOWE (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, III, 13—18. Compare Ruttan and Roebuck, A., 1916, i, 115).—The 1:2- and 1:3-dihydroxypropanes may be directly esterified at high temperatures if constantly stirred, the optimum temperature of esterification varying with the acid used. After fusion, the mixture is freed from glycol by washing with hot water and from free acid by means of sodium hydrogen carbonate. The mono- and di-acid esters are separated by means of their different solubilities in alcohol. The following esters are described:

Propylene monostearate, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, had m. p. $59\cdot5^\circ$, n_D^{60} 1.4424. The *distearate*, m. p. $72\cdot3^\circ$, crystallised in large, flaky crystals, n_D^{75} 1.4366.

Trimethylene monostearate, $\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_{18}\text{H}_{35}\text{O}_2$, had m. p. $60\cdot5^\circ$, n_D^{60} 1.4437, and the *distearate*, m. p. $64\cdot7^\circ$, n_D^{75} 1.4397.

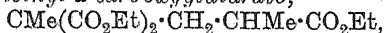
Propylene monopalmitate had m. p. $54\cdot2^\circ$, n_D^{60} 1.4405, and the *dipalmitate*, m. p. $68\cdot8^\circ$, n_D^{75} 1.4364.

Trimethylene dipalmitate had m. p. $56\cdot2^\circ$, n_D^{75} 1.4374. The monopalmitate was not isolated.

W. G.

The Optically Active *aa'*-Dimethylglutaric Acids. ELOF MÖLLER (*Lunds. Univ. Årsskr.*, 1919, 15, 56 pp.; from *Chem. Zentr.*, 1919, i, 606—608).—The author gives two tables of the known optically active dibasic acids with two similarly placed asymmetric carbon atoms, and points out the relationship between melting point and optical activity. There appears to be no connexion between the difference of melting point of the isomerides and the magnitude of the specific rotation. *r-γ*-Dimethylglutaric acid has previously been resolved by means of the strychnine hydrogen salt, but the *L*-isomeride was not obtained pure (A., 1911, i, 12); the two antipodes have now been isolated in a state of purity, fission being effected with brucine or the *α*-phenylethylamines.

Ethyl r-γ-dimethyl-α-carboxyglutarate,



b. p. $156\text{—}158^\circ/15\text{ mm.}$, is prepared by the action of ethyl *β*-bromo-*isobutyrate* on ethyl sodiummalonate; when hydrolysed with sodium hydroxide, it yields *r-γ-dimethyl-α-carboxyglutaric acid* as a sticky mass of indefinite m. p. The saturated aqueous solution contains 159 grams per litre at 20° . The dissociation constant, $100k=0\cdot220$. The *potassium dihydrogen* salt forms long crystals,

the *dipotassium* salt cannot be prepared, whilst the *normal potassium* salt forms small, transparent crystals (+ H_2O). Resolution of the acid could not be effected with α -phenylethylamine, quinine, or cinchonine, but was accomplished through the strychnine dihydrogen salts (the salt of the *d*-acid crystallises in colourless, anhydrous needles, that of the *l*-acid in prisms, + $4\text{H}_2\text{O}$). The active acids have m. p. 144—148°, $[\alpha]_D^{20} + 16.3^\circ$ and -15.6° in aqueous solution, and are more soluble in water than the racemic form.

r- α -Dimethylglutaric acid was partly resolved by strychnine and almost completely by brucine and the α -phenylethylamines, but not by cinchonine, cinchonidine, morphine, or quinine. With molar quantities of strychnine or brucine and *r*-acid, the salts of the *d*-acid separate first. Strychnine *d*- α -dimethylglutarate forms thin, transparent crystals (+ $2\text{H}_2\text{O}$), solubility 2.4 grams in 100 grams water; the corresponding salt of the *l*-acid forms colourless threads, readily soluble in water. The brucine salt of the *d*-acid (+ $2\text{H}_2\text{O}$) crystallises in colourless needles, 0.8 gram of which dissolves in 100 grams of water, whilst the salt of the *l*-acid forms transparent prisms, solubility 1.8 in 100. *l*-Phenylethylamine *d*- α -dimethylglutarate and *d*-phenylethylamine *l*- α -dimethylglutarate crystallise in needles, m. p. 157—158°, solubility 9 grams in 100 grams water; *d*-phenylethylamine *d*- α -dimethylglutarate and *l*-phenylethylamine *l*- α -dimethylglutarate have m. p. 144—145°, solubility 25 in 100. The strychnine salt of the *meso*-acid (+ $2\text{H}_2\text{O}$) forms threads, solubility 12 in 100, whilst the brucine salt dissolves to the extent of 18 parts in 100. *d*- and *l*-Phenylethylamine *meso*- α -dimethylglutarate dissolve freely in water. *d*- and *l*- α -Dimethylglutaric acids crystallise in needles or prisms, $[\alpha]_D^{20} + 39.8^\circ$ in aqueous solution. Examination of the barium hydrogen salt shows that the univalent ion has the same sign of rotation as the parent acid, whilst the bivalent ion of the normal salt is optically inactive. The *l*-anhydride, obtained by the action of acetyl chloride on the *d*-acid at 50—60°, forms cubic crystals, m. p. 41.5—42.5°, $[\alpha]_D^{18} - 69.6^\circ$ in benzene solution, whilst the *d*-anhydride crystallises in slender needles, m. p. 42—43.5°, $[\alpha]_D^{18} + 69.9^\circ$ in benzene solution. The *r*-anhydride, prepared by admixture of its components (the *r*-acid is only attacked by acetyl chloride with difficulty), has m. p. 33—34°.

The product obtained by the elimination of carbon dioxide from optically active α -dimethyl- α -carboxyglutaric acid consists of a mixture of about 40% active and 60% *meso*-dimethylglutaric acid; since the sign of rotation is the same as that of the carboxy-acid, it follows that the tri- and di-basic acids which rotate in the same direction are configuratively related. H. W.

New $\beta\beta$ -Dialkylglutaric Acids. I. GUARESCHI (*Gazzetta*, 1919, 49, i, 124—133. Compare A., 1901, i, 630).—The following further acids have been prepared by the method formerly used:

ββ-Di-n-propylglutaric acid, $\text{CPr}^2(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, prepared from $\alpha\gamma$ -dicyano- $\beta\beta$ -dipropylglutarimide, forms white crystals, m. p. 112—113°, and completely volatilises at a higher temperature, its vapour provoking coughing. The *ammonium* salt is highly soluble in water, its aqueous solutions giving precipitates of various colours with salts of heavy metals.

β-Ethyl-β-propylglutaric acid, $\text{CEtPr}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, crystallises in colourless, flattened needles or long laminae, m. p. 71—72°, and has an intensely acid reaction.

β-Methyl-β-isobutylglutaric acid, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, has m. p. 63—65°.

β-Methyl-β-isoheptylglutaric acid,
 $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CMe}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$,
 forms crystals, m. p. 62—63°; the *silver* and *zinc* salts were analysed.

β-Methyl-β-nonylglutaric acid, $\text{CH}_3 \cdot [\text{CH}_2]_8 \cdot \text{CMe}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, crystallises in broad, colourless laminae, greasy to the feel, m. p. 46·5—47·5°.

β-Methyl-β-hexylglutaric acid, $\text{C}_6\text{H}_{13} \cdot \text{CMe}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$, forms crystals, m. p. 52—53°.
 T. H. P.

Manganous Tartrate and Potassium Manganous Tartrate.

LEONARD DOBBIN (*J. Amer. Chem. Soc.*, 1919, **41**, 934—940).—Manganous tartrate is prepared by adding an equimolecular solution of sodium or potassium tartrate to either manganous sulphate or chloride solutions, when, on keeping, small, rose-tinted crystals separate. The crystals are monoclinic with axial ratios [$\alpha:b:c = 0.816:1:0.699$, $\beta = 100^\circ 14'$]. It loses 14% of its water at 100°, and continues to lose water up to 180°, and at 200° darkens with slight decomposition. The crystals have the formula $\text{MnC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$. All attempts by the author to prepare manganous potassium tartrate failed, hence it appears unlikely that this compound exists.

J. F. S.

New Explosive Substance Derived from Formaldehyde.

ANNIBALE MORESCHI (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 277—280).—The action of dry gaseous hydrogen chloride in the cold on commercial formaldehyde solution (about 40%) in a reflux apparatus yields, first, the compound, $\text{OH} \cdot \text{CH}_2\text{Cl}$. If the action is prolonged, a heavy liquid separates having a composition corresponding with the formula $\text{O}(\text{CH}_2\text{Cl})_2$. Treatment of this liquid at about 5° with a mixture of concentrated nitric and sulphuric acids results in liberation of hydrogen chloride, carbonyl chloride, and probably an oxygenated chlorine acid, and in separation of a colourless oil, D₄ 1.52206, which, from its composition and its cryoscopic behaviour in benzene, appears to have the formula $\text{C}_3\text{H}_4\text{O}_6\text{N}_2$. This compound is extremely sensitive to shock, decomposing with detonation. Of the two possible constitutions, $\text{NO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}$, and $\text{NO}_2 \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{NO}_2$, the latter is the more probable, since hydrolysis leads to the formation of formic

acid and nitromethane. The compound dissolves considerable proportions of cellulose nitrate even at 0°. and an explosive jelly containing 7% of cellulose nitrate (12.11% N) gives a greater increase in volume on explosion than one containing 7% of glyceryl nitrate.

T. H. P.

γ -Hydroxyvaleraldehyde. BURCKHARDT HELFERICH (*Ber.*, 1919, **52**, [B], 1123—1131).—Although α - and β -hydroxy-aldehydes of simple structure have been closely examined, the corresponding γ -derivatives do not appear to have been isolated, although their chemistry is exceptionally important owing to their near relationship to the sugars. The present communication describes an effort to fill this gap.

A solution of methylheptenol in glacial acetic acid is ozonised, diluted with ether and a little water, and treated with zinc dust until the perozonide is reduced; on distillation, a 78% yield of γ -hydroxyvaleraldehyde is obtained. It is a moderately mobile liquid with an odour resembling that of turpentine, b. p. 63—65°/10 mm., D_4^{17} 1.0167, n_D^{17} 1.4359, which mixes with water and organic solvents, but is salted out from its aqueous solution by potassium carbonate, but not by sodium sulphate or chloride. The freshly prepared solution contains the aldehyde in the unimolecular form. The *oxime*, *phenylhydrazone*, and *p-nitrophenylhydrazone* could only be obtained as oils, but the *p-bromophenylhydrazone* forms pale brown crystals, m. p. 88—89° (corr.), after softening at about 85°, and *diphenylmethanedimethyldihydrazone* consists of colourless crystals, m. p. 84—85° (corr.), after slight softening from 80°. The aldehyde yields a *bisulphite* compound, which is readily soluble in water. It does not reduce Fehling's solution in the cold and with only moderate rapidity on heating; ammoniacal silver solution is reduced in the cold. It is converted by concentrated aqueous sodium hydroxide into a crystalline mass, which is transformed into a dark terpinaceous oil when heated. Concentrated hydrochloric acid resinifies the aldehyde slowly in the cold, rapidly when warmed. Treatment of the aldehyde with 1% methyl-alcoholic hydrochloric acid at the ordinary temperature converts it into 5-methoxy-2-

methyltetrahydrofuran, $\begin{matrix} \text{CH}_2\text{---CHMe} \\ \text{CH}_2\text{---CH(OMe)} \end{matrix} > \text{O}$, a mobile, volatile liquid, b. p. 116—118° (corr.)/755 mm., D_4^{16} 0.9291, n_D^{16} 1.4110, which does not reduce boiling Fehling's solution and only reacts slowly with boiling ammoniacal silver solution. It is stable towards hot alkali and only slowly hydrolysed by hot acid. It does not appear to be hydrolysed by emulsin. When boiled with acetic anhydride, the aldehyde gives 5-acetoxy-2-methyltetrahydrofuran, mobile liquid, b. p. 73—78°/9 mm., $D_4^{18.2}$ 1.037, $n_D^{18.2}$ 1.4278, which is gradually converted by water at the ordinary temperature into acetic acid and the aldehyde.

H. W.

Preparation of Xylose from Maize Cobs. K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1002—1003).—The method

described by La Forge and Hudson (*J. Ind. Eng. Chem.*, 1918, **10**, 925) is modified by removing the gum by digestion of the broken maize cobs with sodium hydroxide solution (1%) at 100° for one and a-half hours instead of performing the operation in an autoclave at 160°; the residue is hydrolysed by dilute sulphuric acid (4%), and the latter is subsequently removed with barium carbonate. The sugar solution thus obtained is less coloured than that prepared by previous methods, and crystallisation of the xylose takes place with uniform readiness. The yield is 8—10%. [See also, *J. Soc. Chem. Ind.*, 1919, August.] H. W.

New Sugar Isolated from a Sea-weed. EIJI TAKAHASHI (*J. Tokyo Chem. Soc.*, 1919, **40**, 157—166).—The author has isolated a new sugar from the hydrolytic product of the mucilaginous substance formed by boiling seaweed in water. The sugar crystallises from water in rectangular form, thicker in the middle, is exceedingly sweet, is soluble in alcohol, and has m. p. 152—153° and $[\alpha]_D^{20} + 80.75^\circ$. The molecular weight by the cryoscopic method is 179.3. Tests with resorcinol, phloroglucinol, Tollen's and Oshima's reagents show that it is not a ketose, pentose, or methyl-pentose. It yields lævulinic acid, identified as the silver salt, and is thus shown to be a hexose. It strongly reduces Fehling's solution, is fermented by yeast, but not so readily as dextrose, and forms a *hydrazone* in the cold, m. p. 158—160°, which is soluble in methyl and ethyl alcohols and in hot water. The needle-shaped *osazone*, m. p. 193°, is soluble in the two alcohols, but not in water. The *phenylmethylhydrazone*, rectangular plates, has m. p. 191°, and the *p-bromophenylhydrazone*, m. p. 171—172°. Sodium amalgam reduces it to a hexahydric *alcohol*, prisms, m. p. 186—187°. The new sugar is very similar to galactose in specific rotatory power and in the m. p. of the corresponding alcohol, but differs in crystalline form, in failure to yield mucic and saccharic acids by oxidation with nitric acid, and in the m. p.'s of the various hydrazones and in the solubility of the *osazone* in methyl alcohol. From these analyses the author believes the new sugar to be an aldohexose, and names it *floridose*, and its alcohol, *floriditol*. This name is given because the sugar was first isolated from the red sea-weed *Florideae*. Sugars isolated from various sea-weeds, including *Chondrus elatus* Holms, *Ahnfeltia plicata*, and *Iridaea laminarioides* var. *ornucopiae*, are all easily crystallisable and are found to be absolutely identical with floridose. CHEMICAL ABSTRACTS.

The Preparation of Rhamnose. E. P. CLARK (*J. Biol. Chem.*, 1919, **38**, 255—256).—Liquid quercitron extract is hydrolysed by gently boiling with 3% sulphuric acid for half an hour. After removal of the sulphuric acid as barium sulphate, the material is concentrated to a thin syrup and eight volumes of 95% alcohol are slowly added with constant stirring. The filtrate from this precipitation is evaporated to a thick syrup under diminished pressure and the residue is dissolved in 95% alcohol. On the addition of 2½ volumes of ether, a gummy substance is precipitated.

which is redissolved in alcohol and again precipitated by ether. From the extracts, on removal of the ether and concentration, rhamnose may be crystallised out. The yield is 50--51 grams of white rhamnose from 2 kilos. of the commercial quercitron extract.

J. C. D.

The Constitution of the Disaccharides. Part III. Maltose.

WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1919, 115, 809—817).

Improvements Relating to the Preparation of Amines.

WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES Co., LTD. (Brit. Pat., 127740).—Tertiary amines are separated from admixture with primary and secondary amines by converting the latter into the corresponding urethanes by treatment with ethyl chloroformate in the cold in presence of aqueous sodium carbonate. The unchanged tertiary base is removed from the residual, oily product by washing with dilute mineral acid, and is recovered by treatment of the acid washings with alkali, whilst the primary and secondary bases are regenerated by the hydrolysis of the urethanes. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

G. F. M.

Polypeptides containing Glutamine and the Question of the Occurrence in Proteins.

H. THIERFELDER and E. VON CRAMM [with ALFRED WALTHER] (*Zeitsch. physiol. Chem.*, 1919, 105, 58—82).—It has been suggested that glutamine and asparagine are components of protein rather than glutamic and aspartic acids (Osborne and Gilbert, A., 1906, i, 324; Osborne, Leavenworth, and Braunleht, A., 1909, i, 72).

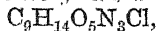
A study of the formation of ammonia during the acid hydrolysis of gliadin, polypeptides containing glutamine, and glutamine itself leads the authors to support the view that glutamine is a component of the protein molecule.

The preparation of four dipeptides and of one tripeptide containing glutamine is described.

Chloroacetyl-d-glutamine, $C_7H_{11}O_4N_2Cl$, fine needles from ethyl acetate, m. p. 130—132°, $[\alpha]_D^{16} = -10.33$ to -10.45° .

Glycyl-d-glutamine, $C_7H_{13}O_4N_3$, crystallises with one molecule of water, and decomposes at 199—200°, $[\alpha]_D^{19} = -2.47^\circ$. This dipeptide has an acid reaction. It is precipitated by phosphotungstic acid, but is soluble in excess, and gives no biuret test.

Chloroacetyl-d-glutaminylglycine ethyl ester, $C_{11}H_{18}O_5N_3Cl$, needles, m. p. 198°. *Chloroacetyl-d-glutaminylglycine*,



needles, m. p. 162—163°. *Glycyl-d-glutaminylglycine*, $C_9H_{16}O_5N_4$, needles, decomposes at 201°, $[\alpha]_D^{19} = -28.4^\circ$. This tripeptide possesses an acid reaction, and is precipitated by phosphotungstic acid, but the precipitate is soluble in an excess of the reagent. It is not precipitated by mercuric chloride, tannic acid, phosphomolybdic acid, basic lead acetate, or saturated ammonium sulphate solution. It gives a bluish-violet biuret reaction.

d- α -Bromopropionyl-d-glutamine, $C_8H_{13}O_4N_2Br$, m. p. 156—157°, $[\alpha]_D^{19} = +9.03$ —9.3°. *d*-Alanlyl-d-glutamine, $C_8H_{15}O_4N_3$, prisms, m. p. 222° (decomp.), $[\alpha]_D^{18} = -9.2^\circ$. It possesses an acid reaction to litmus and gives no biuret test.

l- α -Bromopropionyl-d-glutamine, $C_8H_{13}O_4N_2Br$, rosettes of needles, m. p. 132°. When recrystallised from ethyl acetate the substance gave a rotation in methyl alcohol of $[\alpha]_D^{19} = -17.42^\circ$. The substance, recrystallised from water, gave in the same concentration $[\alpha]_D = -16.4^\circ$. No explanation is put forward. *l*-Alanlyl-d-glutamine, $C_8H_{15}O_4N_3$, needles, m. p. 212—213°, $[\alpha]_D^{18} = -20.1^\circ$. This substance is acid to litmus and gives no biuret reaction.

d- α -Bromoisohexoyl-d-glutamine, $C_{11}H_{19}O_4N_2Br$, m. p. 150°, $[\alpha]_D^{19} = +20.8^\circ$, $[\alpha]_D^{25} = +20.55^\circ$, crystallises in prisms. *l*-Leucyl-d-glutamine, $C_{11}H_{21}O_4N_3$, needles, m. p. 235—236°, $[\alpha]_D^{18} = +12.6^\circ$. It is acid to litmus and gives no biuret reaction. J. C. D.

Catalytic Action of Hydrogen Peroxide on Potassium Ferro- and Ferri-cyanides. E. Lück (*Apoth. Zeit.*, 1919, 34, 87; from *Chem. Zentr.*, 1919, i, 610—611).—If an aqueous solution of potassium ferricyanide is warmed for about two minutes at 45° with 10% of hydrogen peroxide and allowed to cool, almost black crystals, $2K_3FeC_6N_6 \cdot 3H_2O_2$, are obtained which are very sparingly soluble in water, mol. wt. 759.82. In a similar manner, potassium ferrocyanide gives the compound, $2K_4FeC_6N_6 \cdot 3H_2O_2$. H. W.

Modified Graphic Formulæ for Organic Cyclic Compounds.

ALEXANDER LOWY (*J. Amer. Chem. Soc.*, 1919, 41, 1029—1030).—The author recommends the advisability of indicating the double bonds in cyclic compounds by heavy lines and the single bonds by light lines. A series of typical examples is given.

H. W.

Freezing-point Curves of Mixtures of Nitro- and Dinitrobenzene. K. LEHMSTEDT (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, 13, 118—119; from *Chem. Zentr.*, 1919, i, 708).—The author has determined the freezing point of various solutions of pure *m*-dinitrobenzene and of a mixture of *o*-, *m*-, and *p*-dinitrobenzene (6.5%, 92.0%, and 1.5% respectively) in nitrobenzene. The composition of nitrated products can be readily elucidated from the freezing-point curve for the pure dinitrobenzene and for the technical mixture of isomerides. The curve has two eutectic points, probably due to the fact that solutions which contain little dinitrobenzene are not caused to crystallise by seeding with dinitrobenzene. H. W.

The Reduction of 2:3-, 3:4-, and 2:5-Dinitrotoluenes.

JAKOB MEISENHEIMER and ERICH HESSE (*Ber.*, 1919, 52, [B], 1161—1177).—Some years ago (A., 1904, i, 150; 1906, i, 642) it was shown that *o*- and *p*-dinitrobenzenes are converted by cautious reduction in alkaline solution into dark-coloured salts of diacidodinitrocyclohexadienes, which, when acidified, rapidly pass into

nitronitrosobenzenes. The experiments with *o*-dinitrobenzene have been repeated on a large scale, the products now obtained being *o*-nitronitrosobenzene (19% of that theoretically possible), nitrobenzene (31%), *o*-nitrophenol (14%), a little *o*-nitroaniline, and resinous matter.

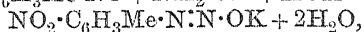
The work has also been extended to 2:3-, 3:4-, and 2:5-dinitrotoluenes, which are found to behave in a precisely similar manner.

3:4-Dinitrotoluene, m. p. 59—60°, is conveniently prepared by oxidising 3-nitro-*p*-toluidine by means of Caro's acid to 3-nitro-4-nitrosotoluene, and completing the oxidation of the latter with nitric acid. Reduction of 3:4-dinitrotoluene by hydroxylamine is effected in the usual manner, but the salt which is produced cannot be isolated on account of its ready solubility. On acidification, the following substances are obtained: 3-nitro-4-nitrosotoluene, m. p. 143°; 4-nitro-3-nitrosotoluene, yellow leaflets, m. p. 141°; a mixture of *m*- and *p*-nitrotoluenes, *p*-nitro-*m*-cresol, m. p. 56°, and resinous products, from which nothing definite could be isolated. Potassium diaci-3:4-dinitromethyl- $\Delta^{1:5}$ -cyclohexadiene is prepared by the addition of an ethereal solution of potassium ethoxide to a suspension of 3-nitro-4-nitrosotoluene in ether, and forms an amorphous powder of dark red colour which is extraordinarily sensitive to moisture; when treated with aqueous acid, it yields a mixture of nitronitrosotoluenes.

2:3-Dinitrotoluene, m. p. 96—97°, is best obtained by the nitration of acet-*o*-toluide by nitric acid in the presence of acetic acid, and decomposition of the mixture of 3- and 5-nitroacet-*o*-toluides with hydrochloric acid; the separation of the isomeric amines is accomplished by diluting the acid solution largely with water, when the very feebly basic 3-nitro-*o*-toluidine is precipitated; the latter is converted by Caro's acid into 3-nitro-2-nitrosotoluene, pale yellow leaflets, m. p. 126—127° (decomp.), which is transformed by nitric acid into 2:3-dinitrotoluene. (6-Nitro-2:4'-dimethylazobenzene, red prisms, m. p. 65.5—66°, is obtained by condensing 3-nitro-2-nitrosotoluene with *p*-toluidine in glacial acetic acid solution; if aniline is used, 6-nitro-2-methylazobenzene is obtained as a red oil, b. p. 215°/11 mm., which does not solidify after many months.) Reduction of 2:3-dinitrotoluene with hydroxylamine follows the normal course, yielding 2-nitro-3-nitrosotoluene, yellow leaflets, m. p. 92—93°, a mixture of *o*- and *m*-nitrotoluenes, and 3-nitro-*o*-cresol, m. p. 69—70°. The potassium salt of diaci-2:3-dinitromethyl- $\Delta^{4:6}$ -cyclohexadiene is prepared from 3-nitro-2-nitrosotoluene, and is very sensitive to moisture.

5-Nitro-2-nitrosotoluene, almost colourless crystals, m. p. 143—144°, is obtained by the action of Caro's acid on the corresponding amine (it condenses with aniline to yield 4-nitro-2-methylazobenzene, red prisms, m. p. 98—99°), and is readily transformed into 2:5-dinitrotoluene, m. p. 50—51°. The latter is reduced by hydroxylamine, and the solution yields on acidification 5-nitro-2-nitrosotoluene and dinitroazoxytoluene, dark brown prisms, m. p. 188—189°. The potassium salt of diaci-2:5-dinitro-

methyl-Δ^{3.6}-cyclohexadiene is obtained as with the other isomerides, and forms an unstable, red salt, which, when acidified, gives dinitro-azoxytoluene. When reduction of 2:5-dinitrotoluene by hydroxylamine is effected in highly concentrated solution, *potassium nitrotolueneisodiazotate*, $C_7H_5O_3N_3K \cdot H_2O$, is precipitated in yellow needles, m. p. 202° (decomp.); the substance owes its origin to the action of hydroxylamine on the intermediately formed nitroso-derivative, $NO_2 \cdot C_6H_3Me \cdot NO + NH_2 \cdot OH + KOH =$



as is shown by its formation by the interaction of hydroxylamine with 5-nitro-2-nitrosotoluene. Attempts are also described to prepare it by the diazotisation of 5-nitro-*o*-toluidine and treatment of the product with sodium hydroxide solution, but the yellow, crystalline material exploded with great violence. H. W.

Preparation of Liquid Hydrocarbons by the Action of Aluminium Chloride on Naphthalene under Pressure.

FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 237—244; from *Chem. Zentr.*, 1917, ii, 584).—[With WILHELM SCHNEIDER.]—A mixture of naphthalene (100 grams) and powdered aluminium chloride (4 grams), when boiled under reflux during three hours and subsequently distilled, yielded about 47 grams of naphthalene impregnated with oil and a residue of 47 grams of a brittle pitch which, when heated to redness, gave a small amount of viscous distillate and much coke. On the other hand, when naphthalene (250 grams) and aluminium chloride (10 grams) were heated under pressure (up to ten atmospheres) at 330° during twenty minutes, 124.5 grams of oil containing naphthalene and 108 grams of charred matter were obtained, from which 92 grams of non-solidifying oil were isolated by freezing and pressing. It is therefore possible to convert technically pure naphthalene by 4% of aluminium chloride in autoclaves into a mixture of liquid hydrocarbons, the yield of which is 40%; the remainder of the naphthalene is converted into a mixture of pitch and carbon, since a portion of the naphthalene is hydrogenated at the expense of the other portion.

[With SIEGFRIED HILPERT.]—1055 Grams of non-solidifying oil were obtained from 3250 grams of naphthalene and 130 grams of aluminium chloride; after treatment with calcium oxide to remove hydrogen chloride, the oil was distilled, and yielded 4% b. p. below 150° , 79% b. p. 150 — 300° , and 16% residue of higher b. p. The chief fraction, when cooled to 0° , deposited 27% of its weight of naphthalene, so that the remainder, which had b. p. 150 — 300° and did not solidify at 0° , constituted 57% of the total oil, or 18% of the original naphthalene. The middle fraction contained 8.4% of hydrogen and 91.5% of carbon. Its heat of combustion was 9932 Cal. (naphthalene, 9628 Cal.; dihydronaphthalene, 10,092 Cal.). The viscosity in Engler's apparatus was 1.16 at 20° and the flash point 70° (Pensky Martens), 75° (open test). The hydrogenated naphthalene could not be burnt in ordinary petroleum lamps without formation of soot. H. W.

Preparation of Thickening Material for Lubricating Oils from Naphthalene. FRANZ FISCHER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 254; from *Chem. Zentr.*, 1919, ii, 584).—Complex compounds, formed by the condensing action of aluminium chloride, remain undecomposed when naphthalene and aluminium chloride are heated at a moderate temperature (compare preceding abstract). Thus, when crude naphthalene (500 grams) is heated in an autoclave with aluminium chloride (50 grams) (the maximum temperature and pressure being respectively 55° and two atmospheres) and the product is distilled with steam, a black, syrupy, viscous residue remains which, after being filtered through cloth while hot, gives with three parts of a fatty tar oil, a black lubricating oil of good quality. H. W.

Conversion of Naphthalene into Liquid Products. HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 255—258; from *Chem. Zentr.*, 1919, ii, 584—585. Compare preceding abstracts).—Attempts have been made to methylate naphthalene by heating it with polymethylbenzenes in the presence of aluminium chloride, since this substance not infrequently causes a wandering of the methyl groups in methylbenzenes. When xylene, b. p. 134—135°, was heated to boiling with aluminium chloride for three hours, a mobile, dark brown, and a viscous, black oil were obtained from the former, of which fractions boiling below and above xylene were isolated. Noticeable action did not occur when dry hydrogen chloride was passed through a suspension of dry aluminium hydroxide in xylene. Under similar conditions, solvent naphtha (25 grams, b. p. 150—175°) yielded fractions, b. p.'s 145—150° (2 grams), 150—175° (15 grams), 175—205° (3 grams), whilst the residue after decomposition with hydrochloric acid gave 2 grams, b. p. 150—280°. A mixture of naphthalene and xylene yielded an oil, b. p. 125—220°, which partly solidified, whilst a mixture of naphthalene and solvent naphtha gave small fractions, b. p.'s 110—150° and 150—175°, and a larger fraction, b. p. 175—225°, consisting of naphthalene impregnated with oil. When naphthalene was boiled with aluminium chloride (4%) during one and a-half hours, and the product treated with hot dilute hydrogen chloride and distilled, oily naphthalene was obtained at 210—225°, and a substance, which solidified to a yellow, waxy mass when the distillation was continued to 220° in an absolute vacuum.

Acenaphthene when boiled with aluminium chloride (4%) for one and a-half hours yielded a yellowish-green, fluorescent oil, b. p. 195—265°, which remained liquid at the ordinary temperature, but deposited acenaphthene at 0°. Similarly, anthracene gave an oil, b. p. 200—300°, which formed a mass of orange crystals at the ordinary temperature, whilst phenanthrene yielded a yellowish-green, fluorescent oil, which partly solidified at 0° and became liquid again at the ordinary temperature. H. W.

Conversion of Naphthalene into Liquid Products by Alkylation. FRANZ FISCHER and WILHELM SCHNEIDER (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 227—230; from *Chem. Zentr.*, 1919, ii, 585. Compare preceding abstracts).—The object of the investigation was the technical liquefaction of naphthalene by alkylation in the simplest possible manner. Naphthalene (5 grams) when heated with absolute alcohol (4.5 c.c.) and zinc chloride (10 grams) at 290—300° during thirty-six hours yielded 0.2 gram of recovered naphthalene and 5.1 grams of a reddish-brown oil with a green fluorescence. By treatment of crude naphthalene (100 grams) with alcohol (96%, 120 c.c.) and zinc chloride (200 grams regenerated, 200 grams fresh substance) at 180—190° during sixty hours it gave 112 grams of a dark brown oil with a green fluorescence which, on distillation, yielded a small fraction, b. p. below 240°, 98 grams of a volatile, yellow oil, b. p. 240—300°, and 12 grams of dark brown, viscous, residual oil; naphthalene did not separate from these oils when cooled with ice-water. The zinc chloride cannot be replaced by granulated calcium chloride, sulphuric acid, sodium hydrogen sulphate, or anhydrous magnesium chloride. When naphthalene (5 grams) was heated with methyl alcohol (3.3 c.c.) and zinc chloride (10 grams) at 290—300° during twelve hours, 3.8 grams of oil were obtained, together with 0.8 gram of naphthalene. A mixture of naphthalene and phenol when heated with zinc chloride at 290—300° gave a considerable amount of carbon and large amounts of unchanged substances. Acetone appeared to react with naphthalene in the presence of zinc chloride with elimination of water. Acetylene and ethylene did not react with naphthalene at 100—200° in the presence of aluminium chloride.

H. W.

Conversion of Naphthalene into Liquid Products by Hydrogenation in Pressure Furnaces in the Presence of Non-metallic Catalysts. FRANZ FISCHER and HERMANN NIGGEMANN (*Ges. Abhand. Kennt. Kohle*, 1917, 1, 231—236; from *Chem. Zentr.*, 1919, ii, 585—586).—The experiments were performed in an electrically heated, horizontal furnace capable of withstanding high pressures. Naphthalene was found to be very resistant to high temperatures, and, except for slight discoloration and traces of separation of carbon, remained unchanged when heated during one hour at 500° in the presence or absence of copper, iron, coke, or selenium; in the presence of 1% of iodine, it became intensely black, owing to separation of carbon. The best conditions for obtaining liquid products from naphthalene by hydrogenation consist in employing high temperatures and pressures. In the absence of catalysts or in the presence of selenium, the liquefaction is minimal. Iodine, on the other hand, is an active catalyst; naphthalene is completely liquefied by heating with 1% of iodine at 550° for one hour in an atmosphere of hydrogen (pressure to about 170 atmospheres) to an oil with a

blue fluorescence, a mirror of carbon being also formed. Carbonisation occurs more readily at high than at low pressures; separation of carbon at a hydrogen pressure less than 50 atmospheres does not occur below 800°, with 50 atmospheres at 800°, with 100 atmospheres at 550°, with 170 atmospheres below 550°. The hydrogenated oils solidify more or less completely after a few days, probably owing to oxidation and separation of dissolved naphthalene. H. W.

Constitution of certain Polynitro-compounds. J. BISHOP TINGLE and WALTER ALBERT LAWRENCE (*Trans. Roy. Soc. Canada*, 1918, [iii], 12, III, 7—11).—The authors have determined the constitution of the nitration products of picranilide and diphenylamine obtained by Tingle and Blanck (compare A., 1908, i, 778), and shown by Tingle and Burke to be tetranitrodiphenylamines (compare A., 1910, i, 21). By the action of nitric acid on picranilide in the presence of oxalic acid, the product obtained is 2:4:6:4'-tetranitrodiphenylamine, m. p. 216°. By the action of trichloroacetic and nitric acids, picranilide yields *s*-tetranitrodiphenylamine, m. p. 191°, together with some bis-2:4-tetranitrodiphenylamine, m. p. 179—180°. On nitrating diphenylamine itself, three compounds are obtained, namely, *s*-tetranitrodiphenylamine as the main product, together with a small quantity of a *tetranitrodiphenylamine*, m. p. above 250°, and a *compound*, not identified. W. G.

Salts of Hexanitrodiphenylamine. H. KAST and A. LANGHANS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1919, 14, 1—4, 25—27; from *Chem. Zentr.*, 1919, i, 719).—The acidic character of hexanitrodiphenylamine, due to the presence of the imide-hydrogen atom, enables it to form soluble salts of orange-yellow to blood-red colour. Readiness of salt formation is considerably restricted by the sparing solubility of the parent substance. A series of salts has, however, been prepared by agitating and warming an aqueous or alcoholic solution or suspension of the requisite metallic oxides, hydroxides, or carbonates with hexanitrodiphenylamine. The *magnesium* salt is the most readily soluble, and may conveniently be used in obtaining the salts of the heavy metals by double decomposition. The salts, with the exception of those of magnesium and ammonium, are more sensitive than the parent substance. The lead salt is the most sensitive, followed in order by the copper, sodium, iron, potassium, calcium, and ammonium salts. The sequence, with the exception of the sodium salt, is therefore the same as with the salts of picric acid and trinitrocresol. H. W.

Preparation of Hexanitrodiphenylamine from Chlorobenzene. E. J. HOFFMAN and PERRY A. DAME (*J. Amer. Chem. Soc.*, 1919, 41, 1013—1020).—The preparation is effected in the following stages; (i) nitration of chlorobenzene to chlorodinitro-

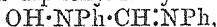
benzene by a mixture of nitric and sulphuric acids, (ii) formation of dinitrodiphenylamine by heating chlorodinitrobenzene with aniline, (iii) preparation of tetranitrodiphenylamine by the action of nitric acid on the dinitro-compound (compare Carter, *Zeitsch. ges. Schiess. Sprengs.*, 1913, **8**, 205, 251), and (iv) conversion of tetranitrodiphenylamine into hexanitrodiphenylamine by nitric-sulphuric acid, the latter procedure being a modification of Carter's method. The best experimental conditions for each stage are fully described, and the yield of hexanitro-derivative is 68.62% of that theoretically possible, calculated on the basis of chlorobenzene used. The authors' results lead them to the conclusion that the intermediate isolation of the tetranitro-compound is probably unnecessary, and that the dinitro- can be converted directly into the hexanitro-derivative. The latter crystallises in fine, yellow needles, m. p. 240—250° (decomp.). It is a very brisant explosive, scarcely suitable for explosive purposes except when mixed with other substances. It is much more poisonous than glyceryl nitrate, and causes severe blisters, resembling burns, when it comes in contact with the skin. The fine dust especially affects destructively the mucous membranes of the mouth, nose, and lungs. H. W.

Catalytic Hydrogenation of Schiff's Bases. ALPH. MAILHE (*Bull. Soc. chim.*, 1919, [iv], **25**, 321—325).—Schiff's bases, obtained by condensing an aldehyde with a primary amine, readily undergo hydrogenation when passed with hydrogen over reduced nickel at 200—230°, giving the corresponding secondary amine. At the same time, there is a slight secondary reaction, represented by the equation $R \cdot CH : NR' + 2H_2 = R \cdot CH_2 + R' \cdot NH_2$. Satisfactory yields were obtained in this manner from five of these bases. W. G.

N-Phenylhydroxylamine and Methyl Sulphate. EUG. BAMBERGER and ALEXANDER LANDAU (*Ber.*, 1919, **52**, [B], 1093—1110).—Since previous attempts to prepare alkyl derivatives of N-phenylhydroxylamine by means of methyl iodide, methyl bromide, or diazomethane did not give the desired result, the authors have examined the action of methyl sulphate without, however, being able to effect the isolation of the ethers.

The majority of the experiments were performed by adding methyl sulphate and sodium hydrogen carbonate to an aqueous solution or suspension of phenylhydroxylamine at 0°. In these circumstances the most readily isolable product is the methylenediphenylhydroxylamine, $CH_2(NPh \cdot OH)_2$, which had previously been obtained by the use of diazomethane as methylating agent (Bamberger and Tschirner, A., 1900, i, 342). In addition, small quantities of azoxybenzene, aniline, and mono- and di-methyl-anilines were isolated, but it is uncertain whether the latter were produced by the methylation of aniline or by the decomposition of phenylmethylhydroxylamine. The methylene-diphenylhydroxylamine was accompanied by a second base which was without doubt formed from it during its purification, and which was identified as glyoxime-N-phenyl ether, $O : NPh : CH - CH : NPh : O$. Small amounts

of oily and crystalline substances were also produced, but in quantity scarcely sufficient for complete identification. Among these was a substance crystallising in colourless leaflets, m. p. about 132° (which closely resembled diphenyl-*N*-hydroxyformamidine,



but complete identity could not be established), a product, m. p. 232°, and an impure oil which possibly contained phenylmethylhydroxylamine. Since the total weight of these products did not correspond with the amount of material employed, the residual aqueous solution was treated with sulphuric acid and sodium nitrite, when *p*-nitrodimethylaniline, m. p. 162°, and *o*-nitrodimethylaniline were obtained. The only probable source of these substances was dimethylaniline *N*-oxide, which was actually isolated in the form of its picrate; it is remarkable that the amount of the latter generally appears to increase when the reaction mixture is preserved.

When phenylhydroxylamine and methyl sulphate were mixed, the reaction became extremely violent after a short time; in the presence of ether as diluent, the action could be conveniently regulated and the products were dimethylaniline oxide, methylenedi-phenylhydroxylamine, small quantities of aniline, and the methylanilines and substances of unknown composition. A portion of the phenylhydroxylamine was removed from action in the form of its methosulphate. In addition, a reddish-brown oil was obtained which possibly contains phenylhydroxylamine *O*-methyl ether.

Attempts were also made to use nascent phenylhydroxylamine by reducing nitrobenzene with zinc and ammonium chloride in the presence of methyl sulphate; the products, however, were the same as those obtained previously.

The production of methylenedi-phenylhydroxylamine during the methylation of phenylhydroxylamine is explained in the following manner: the primary product of the change is phenylmethylhydroxylamine, which spontaneously decomposes into formaldehyde and aniline, $\text{Ph}\cdot\text{NMe}\cdot\text{OH}=\text{CH}_2\text{O}+\text{PhNH}_2$; the formaldehyde then condenses with more phenylhydroxylamine to yield methylenedi-phenylhydroxylamine. The conversion of the latter by boiling water or alcohol into glyoxime-*N*-phenyl ether depends on its hydrolysis to formaldehyde and *N*-phenylhydroxylamine and reaction between these substances: $\text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{OH}+\text{H}_2\text{O}=\text{CH}_2\text{O}+2\text{NHPH}\cdot\text{OH}$ and $2\text{CH}_2\text{O}+2\text{NHPH}\cdot\text{OH}=\text{O}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}+2\text{H}_2\text{O}+\text{H}_2$. In an intermediate stage the formaldehyde condenses under the basic influence of phenylhydroxylamine to glycollaldehyde,

which reacts thus: $\text{OH}\cdot\text{CH}_2\cdot\text{CHO}\xrightarrow{\text{NHPH}\cdot\text{OH}}\text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CHO}$ or $\text{OH}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}\rightarrow\text{O}\cdot\text{NPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{NPh}\cdot\text{O}+\text{H}_2$. The liberated hydrogen is used in the reduction of a further molecule of phenylhydroxylamine.

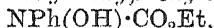
H. W.

Attempts to Prepare β -Phenylhydroxylamine *O*-Methyl Ether. EUG. BAMBERGER (*Ber.*, 1919, 52, [B], 1111—1123).—Attempts to prepare the substance by the action of methyl iodide or

methyl bromide under widely varied conditions did not lead to the desired result, the products generally consisting of azoxybenzene, azobenzene, aniline, and methylaniline. Similarly, the product could not be obtained by the hydrolysis of *N*-benzoylphenylhydroxylamine *O*-methyl ether or of phenyloxyurethane *O*-methyl ether. Apparently, phenylhydroxylamine *O*-methyl ether dissociates with extreme readiness under the influence of hydroxyl ions into $\text{PhN}^<$ (or azobenzene) and methyl alcohol.

[With K. BLASKOPF and ALEXANDER LANDAU.]—*N*-Benzoylphenylhydroxylamine and dibenzoylphenylhydroxylamine are prepared by the action of benzoyl chloride on an aqueous solution of phenylhydroxylamine in the presence of sodium hydrogen carbonate or sodium acetate, and are conveniently separated by taking advantage of the solubility of the former and insolubility of the latter in aqueous ammonia; they form colourless needles, m. p. 121–122°, and shining needles, m. p. 117–118° respectively. *N*-Benzoylphenylhydroxylamine *O*-methyl ether, cubic crystals, m. p. 54.5–55°, is prepared by the action of methyl iodide and sodium methoxide on the mono-benzoyl compound or, more conveniently, by the methyl sulphate method. When hydrolysed with boiling methyl-alcoholic potassium hydroxide, it yields azobenzene; with aqueous alkali in the presence of acetone, it gives benzoic acid, azobenzene, aniline, and, possibly, *p*-anisidine; with aqueous alkali the chief products are benzoic acid and azobenzene. Benzoic acid, *p*-aminophenol, aniline, and *p*-anisidine are formed when sulphuric acid and methyl alcohol are used, whilst when the latter is replaced by ethyl alcohol *p*-phenetidine is produced.

[With F. TSCHIRNER.]—*Hydroxyphenylurethane*,



colourless, silky prisms, m. p. 47.5°, is prepared by the action of ethyl chloroformate on an ethereal solution of phenylhydroxylamine (the sodium derivative forms fine, colourless crystals), and is reduced by zinc dust and acetic acid to phenylurethane, m. p. 51°. *m*-Tolylhydroxyurethane is similarly prepared and has m. p. 30°. When treated with methyl iodide and potassium methoxide, phenylhydroxyurethane is converted into *methoxyphenylurethane*, mobile oil, b. p. 124°/12 mm. The latter is hydrolysed by aqueous ammonia, yielding, as main products, ethylurethane and azobenzene.

H. W.

Preparation of Acyl Derivatives of a *p*-Aminophenyl Ether. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 310967; from *Chem. Zentr.*, 1919, ii, 422–423).—*p*-Aminophenyl allyl ether is caused to react with aliphatic acids, acid anhydrides, or acid haloids if necessary in the presence of a suitable diluent or condensing agent. *p*-Acetylaminophenyl allyl ether, shining leaflets, m. p. 94°, is thus obtained by boiling the amino-ether with acetic anhydride. *Lactylaminophenyl allyl ether*, from the amino-ether and lactide at 150°, forms shining leaflets, m. p. 87°. *isoValeryl-p-aminophenyl allyl ether*, small needles, m. p. 95°, is obtained from the acid, whilst *α-bromoisovaleryl-p-aminophenyl allyl ether*, shining

leaflets, m. p. 131° , is prepared from the amino-ether and α -bromo-*isovaleryl* bromide in the presence of ether and sodium carbonate. The substances are powerful soporifics, which also possess sedative and antineuralgic properties. H. W.

***p*-Cymene. II. Utilisation of Cymene for the Preparation of Photographic Developers.** HERBERT A. LUBS (*J. Ind. Eng. Chem.*, 1919, 11, 455—456. Compare Andrews, A., 1918, i, 339).—Cymene is nitrated and the nitro-derivative reduced to 4-*isopropyl-o*-toluidine (*ibid.*), which is converted through the diazo-reaction into carvacrol. This is transformed into the *p*-nitroso-compound by adding sodium nitrite to an alcoholic solution of the phenol, saturated with hydrogen chloride, and the product is dissolved in 10% ammonia solution and reduced by hydrogen sulphide, when *p*-aminocarvacrol [$\text{Me}:\text{Pr}:\text{OH}:\text{NH}_2=1:4:2:5$] is precipitated in colourless leaflets. This is a better developer than *p*-aminophenol and gives as good tones as metol, but it does not keep quite so well as this in the developing bath.

Thymoquinol may also be made from sulphonated carvacrol, but the yields are poor and it offers no advantages over quinol. *p*-Aminothymol is also not a suitable developer. J. C. W.

3-Nitro-*o*-toluic Acid. S. GABRIEL and ARTHUR THIEME (*Ber.*, 1919, 52, [B], 1079—1092).—3-Nitro-*o*-toluic acid, the last of the ten theoretically possible nitrotoluic acids, has been recently described by Mayer (A., 1915, i, 958); the authors find that some of his data are incorrect, and have re-investigated the substance.

Acet-*o*-toluidide is converted by nitric acid in acetic acid solution in the presence of acetic anhydride into a mixture of 3- and 5-nitro-acet-*o*-toluidides, which are hydrolysed with concentrated hydrochloric acid; under suitable conditions, 3-nitro-*o*-toluidine can be precipitated from this solution by addition of water, whilst the 5-nitro-isomeride remains dissolved. The former is reduced by hydriodic acid to the corresponding diamine, m. p. $63\text{--}64^{\circ}$, the relative position of the amino-groups following from its transformation into 4(or 7)-methylbenzimidazole, m. p. 145° (*hydrochloride*, rhombic plates which do not melt below 300°). 3-Nitro-*o*-toluonitrile, silvery leaflets, m. p. $109\text{--}110^{\circ}$, is prepared by Sandmeyer's method and treatment of the crude product with alcohol or with nitric acid; it is reduced by hydriodic acid and phosphorus to 3-amino-*o*-toluonitrile, m. p. $127\text{--}128^{\circ}$, which by further application of Sandmeyer's reaction gives 3-methylphthalonitrile, colourless needles, m. p. 143° , from which 3-methylphthalimide, m. p. $189\text{--}190^{\circ}$, is prepared by the action of sulphuric acid. Attempts to hydrolyse 3-nitro-*o*-toluonitrile directly to the acid were unsuccessful, but it is transformed by sulphuric acid into 3-nitro-*o*-toluamide, delicate needles, m. p. 158° , which is readily converted by Bouveault's method into 3-nitro-*o*-toluic acid, long, colourless needles or short rods, m. p. $151\text{--}152^{\circ}$ [the sodium (+ $3.5\text{H}_2\text{O}$), barium (+ $3\text{H}_2\text{O}$)],

and *silver* salts are described]. The acid cannot be directly esterified by methyl alcohol and hydrogen chloride, but the *methyl* (needles and leaflets, m. p. 50°) and *ethyl* (oily) esters are readily prepared by the action of the requisite alcohol on the acid *chloride*, m. p. 41°. 3-Nitro-*o*-toluic anhydride forms six-sided plates, m. p. 174°.

3-Nitro-*o*-toluamide is converted by prolonged treatment with boiling hydriodic acid into carbon dioxide and *m*-toluidine; when reduced with tin and hydrochloric acid it yields 3-methylbenzisoxazole-3-one, slender needles, m. p. 119—120° (decomp.), *m*-toluidine hydrochloride, and 3-amino-*o*-toluic acid hydrochloride; the free acid, needles, m. p. 125—126° (decomp.), may also be prepared by reduction of the nitro-acid with ferrous sulphate in ammoniacal solution. When heated with formamide, it is converted into 5-methylquinazole-4-one, long needles, m. p. 224°.

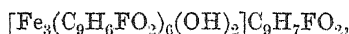
Ethyl nitrotoluoylemalonate, $C_6H_3Me(NO_2) \cdot CO \cdot CH(CO_2Et)_2$, prisms, m. p. 60°, is prepared by the action of 3-nitro-*o*-toluoyl chloride on ethyl sodiomalonate, and yields a *potassium* derivative, $C_{17}H_{16}O_4NK$, yellow, silky needles. When boiled with hydriodic acid and red phosphorus, it gives 2:4-dihydroxy-5-methylquinoline, microcrystalline powder, which does not melt at 300°, and is converted by phosphoryl chloride into 2:4-dichloro-5-methylquinoline, long, slender needles, m. p. 132°. Treatment with tin and fuming hydrochloric acid transforms the dichloro-base into a mixture of 5-methyltetrahydroquinoline hydrochloride, needles and leaflets, m. p. 238—240° (the *nitroso*-derivative of the tetrahydro-base crystallises in shining, oblique prisms, m. p. 69—70°), and 5-methylquinoline, b. p. 263—264°/753 mm., 264—265°/765 mm. (picrate, m. p. 218—219°, methiodide, lemon-yellow needles and plates, m. p. 197° after softening at 193°); the latter base can also be obtained in small yield by distilling 2:4-dihydroxy-5-methylquinoline with zinc dust.

The following details of previously undescribed nitro- and amino-toluenitriles are given. 5-Nitro-*o*-toluenitrile (compare Mayer, *loc. cit.*), prepared from 5-nitro-*o*-toluidine in the manner used for the 3-isomeride, forms colourless leaflets, m. p. 100°, which are readily hydrolysed by a mixture of glacial acetic and fuming hydrochloric acids at 165°, to 5-nitro-*o*-toluic acid, m. p. 152—153°. The nitro-nitrile is readily reduced by stannous chloride and hydrochloric acid to 5-amino-*o*-toluenitrile, rhombic crystals, m. p. 90°. 6-Nitro-*m*-toluenitrile, m. p. 80°, is similarly reduced to 6-amino-*m*-toluenitrile, long, colourless needles, m. p. 95°. 5-Nitro-*m*-toluenitrile, needles, m. p. 104—105°, is prepared by the action of thionyl chloride on the corresponding *amide*, small needles, m. p. 164—165° (from 5-nitro-*m*-toluoyl chloride and ammonia in ethereal solution); 5-amino-*m*-toluenitrile forms needles, m. p. 75° (the *hydrochloride* is slowly volatile at 100°). 2-Nitro-*m*-toluenitrile, m. p. 84°, is reduced by hydriodic acid or ammonium sulphide to 2-amino-*m*-toluamide, m. p. 149°; by stannous chloride and hydrochloric acid to 2-amino-*m*-toluenitrile, m. p. 38°. H. W.

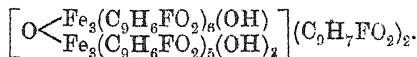
A Novel Application of Bromine Water in Synthetic Organic Chemistry. JOHN READ and MARGARET MARY WILLIAMS (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 558—564).—It has previously been shown (T., 1917, **111**, 240) that ethylene reacts directly with bromine water to give a good yield of ethylene bromohydrin. In the same way when air charged with bromine vapour is passed through a suspension of cinnamic acid in ice-cold water kept well stirred, a yield of over 80% of α -bromo- β -phenyl-hydracrylic acid is obtained, the other product being $\alpha\beta$ -dibromo- β -phenylpropionic acid. If the cinnamic acid is replaced by sodium cinnamate only 53% of the bromohydrin is obtained, and there is a third product, namely, β -bromostyrene, which accounts for 42.6% of the sodium cinnamate used.

W. G.

Fluorocinnamic Acid. F. SWARTS (*Bull. Soc. chim.*, 1919, [iv], **25**, 325—335).—When benzaldehyde is slowly added to methyl fluoroacetate in the presence of sodium, the mixture being cooled below 0°, the principal product is *methyl fluorocinnamate*, m. p. 25°, b. p. 138°/23 mm., $D_{25}^{4.2}$ 1.17258. It is readily saponified by aqueous potassium hydroxide, giving the *potassium salt*, from which, on acidifying, *fluorocinnamic acid*, m. p. 157.6° (corr.), b. p. 290°, is obtained. It yields *calcium*, *barium*, and *silver salts* and two complex *iron compounds* having the composition:



and

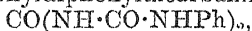


Fluorocinnamic acid is readily brominated, giving *α -fluoro- $\alpha\beta$ -dibromo- β -phenylpropionic acid*, m. p. 161.8°, giving a *barium salt* and a *methyl ester*, m. p. 120° (corr.).

W. G.

Action of Ammonia and Amines on the Substituted Carbamides and Urethanes. I. Carbonyldiurethane. F. B. DAINS, H. W. GREIDER, and C. H. KIDWELL (*J. Amer. Chem. Soc.*, 1919, **41**, 1004—1013).—Carbonyldiurethane, silky needles, m. p. 108°, is readily prepared by the addition of urethane (2 mols.) and pyridine (2 mols.) to a 10% solution of carbonyl chloride in benzene. It does not react with anhydrous liquid ammonia, but, in the presence of a little water, it gives carbethoxybiuret, m. p. 162—163°, traces of biuret, and cyanuric acid. No reaction occurs with cold alcoholic ammonia, but with aqueous ammonia (28%) the main reaction consists in the hydrolysis of one of the carbethoxy-groups, with the resulting production of ethyl allophanate, m. p. 192° (the *silver salt* is described); at the same time, carbethoxybiuret is formed, but, being unstable in the ammonia solution, appears only as its decomposition product, cyanuric acid; biuret is formed only to a very limited extent. Ethyl allophanate is produced in 80% yield when ethylamine is used.

The course of the action of aniline on carbonyldiurethane depends largely on the temperature employed. At 110—115°, the products are diphenylbiuret, m. p. 210°, and phenylcarbethoxybiuret, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, m. p. 174° (the *sodium* and *silver* salts are described); the latter yields alcohol when dissolved in sodium hydroxide, and the solution on acidification gives phenylisocyanuric acid, fine needles, m. p. 290—300° for different preparations, which forms a *silver* and a *copper* salt. (Phenylcarbethoxybiuret and phenylisocyanuric acid, together with phenylurethane and phenylallophanic ester, are produced by the action of phenylcarbimide on urethane at 130°.) At 130—150°, the products are phenylcarbethoxybiuret, diphenylbiuret in a larger yield than before, and carbonyldiphenyldicarbamide,



m. p. 211°. At 170°, a little phenylcarbamide, m. p. 147°, and diphenylcarbamide, m. p. 235°, are also formed, and, at higher temperatures, the latter becomes the main product.

With *o*-toluidine at 130°, phenyldiurethane yields *o*-tolylcarbethoxybiuret, fine, colourless crystals, m. p. 155—156° (from which *o*-tolylisocyanuric acid, colourless needles, which do not melt below 300°, and yield a mono-*silver* salt, is obtained, as with the corresponding phenyl derivative), *di-o*-tolylbiuret, needles, m. p. 202—203°, and ethyl *o*-tolylallophanate, m. p. 137°. At 140°, the products are *o*-tolylcarbethoxybiuret, a little *di-o*-tolylcarbamide, and carbonyldi-*o*-tolyldicarbamide, m. p. 186°. At 170—180°, *di-o*-tolylbiuret, carbonyldi-*o*-tolyldicarbamide, *di-o*-tolylcarbamide, m. p. 248°, and *o*-tolylcarbamide, m. p. 188°, are obtained. *Di-o*-tolylcarbamide is the only substance isolated from experiments at 200°.

At 130—140°, β -naphthylamine yields mainly β -naphthylcarbethoxybiuret, colourless needles, m. p. 196° (β -naphthylisocyanuric acid has m. p. 290—291°), with small amounts of carbonyldi- β -naphthyldicarbamide, m. p. 293°. α -Naphthylamine, on the other hand, yielded at 130° mainly *di- α -naphthylcarbamide*, m. p. 280°; smaller amounts of α -naphthylcarbethoxybiuret, colourless needles, m. p. 198° (α -naphthylisocyanuric acid has m. p. 290°), and of *di- α -naphthylbiuret*, colourless crystals, m. p. 278—279°, were also produced.

The reactivity of carbonyldiurethane appears to be dependent on the presence of the carbonyl group, since neither methylenediurethane nor the substituted methylenediurethanes form metallic salts or react with amines. Thus, methylenediurethane is not attacked by aniline at 130°, traces of ammonia are evolved at 160°, and at 200° only a little diphenylcarbamide is obtained, which results from the slight dissociation of the urethane. The introduction of a phenyl group in the methylene radicle does not increase the reactivity of the substance, and, similarly, *o*-nitrophenylmethylenediurethane, colourless crystals, m. p. 190°, does not give an amide with ammonia or with aniline at temperatures up to 200°.

H. W.

Xylyloxyacetic Acids. W. GLUUD and P. K. BRENER (*Ges. Abhand. Kennt. Kohle*, 1917, 2, 257—260; from *Chem. Zentr.*, 1919, i, 626).—Since the tolyloxyacetic acids are useful in the separation of the cresols of low temperature tars, the authors have investigated the corresponding compounds of the xylenols. *p*-Xylyloxyacetic acid, long, slender needles, m. p. 118°, is obtained in 35% yield by the action of chloroacetic acid on *p*-xylenol in the presence of aqueous sodium hydroxide. The sodium salt is described. 4-*o*-Xylyloxyacetic acid, long, colourless needles or thin, rectangular plates, m. p. 162·5°, is similarly obtained in 63% yield; the sodium salt is crystalline. *m*-Xylyloxyacetic acid, long, white needles, m. p. 141·6°, is prepared in 51·5% yield. Ethyl *p*-tolylloxyacetate is obtained from ethyl chloroacetate and sodium *p*-tolylloxide; it is an oil, b. p. 142—143°/11 mm., which is converted by methyl-alcoholic ammonia into *p*-tolylloxyacetamide, m. p. 128°. H. W.

Trimethylene Disalicylate and Method of Preparing the Same. A. M. CLOVER (U.S. Pat. 1,286,944).—Trimethylene disalicylate, $\text{CH}_2(\text{CH}_2\cdot\text{CO}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH})_2$, is prepared by the esterification of the glycol with twice its weight of salicylic acid in presence of half its weight of concentrated sulphuric acid at a temperature not exceeding 100°. Excess of unchanged acid is removed by washing the product with aqueous sodium carbonate at 50°, and the ester, which solidifies on cooling, is purified by crystallisation. It is a colourless, odourless substance of m. p. 77°, and has anti-rheumatic properties. G. F. M.

Some Aromatic $\beta\gamma$ -Unsaturated Ketonic Acids. R. CIUSA (*Gazzetta*, 1919, 49, i, 164—171).—Descriptions are given of a number of unsaturated ketonic acids, obtained by the condensation of pyruvic acid with aromatic aldehydes, $\text{R}\cdot\text{CHO} + \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} = \text{H}_2\text{O} + \text{R}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CO}_2\text{H}$.

Benzylidenepyruvic acid (compare A., 1910, i, 684) gives with phenylhydrazine a compound, m. p. 163—165° (Erlenmeyer, A., 1903, i, 698, gave m. p. 158°; 1904, i, 500), which dissolves in hot sodium carbonate solution, yields aniline when reduced with sodium amalgam, and is converted by boiling with glacial acetic acid in a reflux apparatus into a compound, m. p. 195° (decomp.), answering to Knorr's pyrazoline reaction; it must, therefore, be regarded as a true phenylhydrazone. The acid yields a dibromide, $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 124° (Erlenmeyer, *loc. cit.*, gave m. p. 138°, decomp.), decomposing at 166°. Benzylidenepyruvic acid *p*-nitrophenylhydrazone gives a crystalline sodium salt, which has been analysed.

Cinnamylidenepyruvic acid (*loc. cit.*; also Erlenmeyer, *loc. cit.*) yields a methyl ester, $\text{C}_{13}\text{H}_{12}\text{O}_3$, m. p. 126°, and a tetrabromide, $\text{CHPhBr}\cdot[\text{CHBr}]_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$, which forms white needles, turning red at 200°. m. p. 218°. The ethyl ester forms (1) a tetrabromide, $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Br}_4$, white needles, m. p. 118°, and a dibromide,

$C_{14}H_{14}O_3Br_2$, yellow needles, m. p. 86° . The phenylhydrazones of the acid and of its ethyl ester exhibit the behaviour of true hydrazones.

m-Nitrobenzylidenepyruvic acid, m. p. 111° (compare Baeyer and Drewsen, A., 1883, 341), forms a *sodium* salt ($+H_2O$) and a *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, which crystallises in long, silky needles, m. p. 64° .

p-Nitrobenzylidenepyruvic acid, $C_{10}H_7O_5N$, forms shining, white needles, m. p. 117° . The *dibromide*, $NO_2 \cdot C_6H_4 \cdot [CHBr]_2 \cdot CO \cdot CO_2H$, crystallises in white needles, m. p. 78° .

Anisylidenepyruvic acid, $OMe \cdot C_6H_4 \cdot CH:CH \cdot CO \cdot CO_2H$, forms yellow needles, m. p. 81° , and crystallises from alcohol with $\frac{1}{3}Et \cdot OH$. Its *sodium* salt and its *dibromide*, $C_{11}H_{10}O_4Br_2$, crystallising in white scales, m. p. 125° , were prepared.

The compound, m. p. $137-138^\circ$, described by Ryan and Dunlea (A., 1913, i, 1067) as 5-phenyl-3-styrylisooxazole is probably the 3-phenyl-5-styrylisooxazole obtained by the author and Terni (A., 1911, i, 918), since the action of hydroxylamine on cinnamoylbenzoylmethane may result in the formation of two isomeric *isooxazoles*.

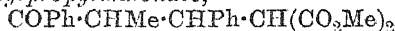
T. H. P.

The Isomeric Tropic Acids. ALEX. MCKENZIE and JOHN KERFOOT WOOD (T., 1919, 115, 828-840).

Preparation of 1:6-Dihydroxynaphthoyl-*o*-benzoic Acid and its Salts. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 311213; from *Chem. Zentr.*, 1919, ii, 586).—1:6-Dihydroxynaphthalene is condensed with phthalic anhydride or phthalic acid in the presence of boric acid, and the acid is converted into its metallic salts by the usual methods; the presence of boric acid causes the reaction to result chiefly in the production of 1:6-*dihydroxynaphthoyl-*o*-benzoic acid*, whilst in the absence of a condensing agent or in the presence of substances such as zinc chloride, phthaleins are mainly or exclusively formed. 1:6-Dihydroxynaphthoyl-*o*-benzoic acid forms coarse crystals, m. p. $226-227^\circ$. The following salts are described: *monosodium* salt, pale yellow, flat prisms; the *disodium* salt is hygroscopic; *monopotassium* salt, yellow, rhombic or prismatic crystals; the *dipotassium* salt is sparingly soluble in alcohol or water; *monocalcium* salt, pale yellow, coarse crystals; *lead* salt, yellow, powdery precipitate; *copper* salt, green powder. 1:6-Dihydroxynaphthoyl-*o*-benzoic acid and its salts have a very sweet taste, whilst the corresponding 1:5-compound and its derivatives are tasteless. The new acid and its salts form a substitute for sugar and other sweetening agents, and also intermediate substances for the manufacture of dyes. When printed, as for chrome colours, 1:6-dihydroxynaphthoyl-*o*-benzoic acid gives bright greenish-yellow shades on cotton and wool which are fast to light and washing, whilst the corresponding 1:5-acid yields orange shades which are much less fast to light. H. W.

The cycloPropane Series. E. P. KOHLER and T. L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 992—1001. Compare A., 1917, i, 566, 570; 1918, i, 72).—One of the most characteristic properties of cyclopropane derivatives is the ease with which the ring is opened by alkyl oxides, with the production of a metallic derivative of an isomeric ethylenic ester. The action has been ascribed to the addition of the alkyl oxide, followed by elimination of alcohol. In the present instance, the behaviour of methyl 2-phenyl-3-methyl-3-benzoylcyclopropanedicarboxylate has been investigated, since the elimination of alcohol is here impossible owing to the presence of the methyl group in position 3; the substance, however, does not appear to be appreciably affected by sodium methoxide.

The condensation of phenyl α -methylstyryl ketone and methyl malonate is best effected by means of a solution of sodium in dry methyl alcohol at the temperature of the steam-bath; the product consists of a mixture of the two stereoisomeric forms of *methyl γ -benzoyl- β -phenylpropylmalonate*,



(m. p.'s 91—93° and 88—90° respectively), in addition to a considerable amount of oil. Each of the esters can be hydrolysed to the corresponding *acid* (m. p. about 160°, and thick needles, m. p. 67°, respectively), from which the *γ -benzoyl- β -phenylvaleric acids* (silky needles, m. p. 115—117°, and small, transparent needles, m. p. 92—93°) are obtained by elimination of carbon dioxide; when treated with methyl alcohol and hydrogen chloride, these two acids yield the same *methyl ester*, large, rhomb-shaped prisms, m. p. 92° (which probably has the same configuration as the dibasic ester, m. p. 92°), whilst with bromine in carbon tetrachloride solution they give *γ -bromo- γ -benzoyl- β -phenylvaleric acid*, fine needles, m. p. about 160° (decomp.), from which *γ -benzoyl- β -phenyl- γ -methylbutyrolactone*, flat, six-sided plates, m. p. 93°, is obtained by the action of sodium carbonate.

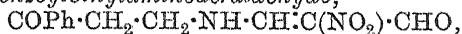
The stereoisomeric methyl *γ -benzoyl- β -phenylpropylmalonates* readily react with bromine, yielding the same products, namely, a small amount of *methyl γ -bromo- γ -benzoyl- β -phenylpropylmalonate*, short, coarse needles, m. p. 114—115°, and an oil; the position of the bromine atom in the solid compound is deduced from its conversion into *methyl- γ -benzoyl- β -phenyl- γ -methylbutyrolactone-carboxylate*, colourless plates, m. p. 85°, when heated, and the identity of this substance with that obtained by the half-hydrolysis of the saturated ketonic ester and the action of bromine on the ester-acid. The action of potassium acetate on methyl *γ -bromo- γ -benzoyl- β -phenylpropylmalonate* yields *methyl 3-benzoyl-2-phenyl-3-methylcyclopropanedicarboxylate*, $(\text{CO}_2\text{Me})_2\text{C} \begin{smallmatrix} \text{CHPh} \\ \text{CMeBz} \end{smallmatrix}$, narrow prisms, m. p. 101°, which is not oxidised by permanganate, but is readily reduced by zinc dust and acetic acid, yielding the saturated ester, m. p. 91—93°, as sole product of the action. The ester acid, unlike the derivatives of cyclopropane previously studied, is insensitive to alkyl oxides except in the presence of moisture,

when it is hydrolysed to the corresponding *acid ester*, three-sided prisms, m. p. 162°. 3-Benzoyl-2-phenyl-3-methylcyclopropanedicarboxylic acid, needles, m. p. 176—178° (decomp.), is obtained by complete hydrolysis of the corresponding ester, into which it is reconverted through the silver salt; when treated with methyl alcohol and hydrogen chloride, on the other hand, the sole product is a very stable, crystalline compound, $C_{22}H_{26}O_7$, m. p. 158.5—159.5°.

The oily material obtained during the bromination of the methyl γ -benzoyl- β -phenylpropylmalonates was treated with potassium acetate, whereby a small further quantity of the cyclopropane ester already described, and an ethylenic isomeride, stout needles, m. p. 129—131°, were isolated; the latter is not reduced by zinc dust and acetic acid, and hence is not a cyclopropane derivative. Its most characteristic property is the readiness with which it is transformed by bases or mineral acids into an isomeric *ester*, hexagonal plates, m. p. 145°. On hydrolysis, it yields an *ester acid*, needles, m. p. about 189° (decomp.), and a dibasic acid, needles, m. p. about 180° (decomp.); these compounds, however, are probably derivatives of the ester, m. p. 145°, since this ester is obtained when the acid is esterified either by the silver salt method or by methyl alcohol and hydrogen chloride. H. W.

Condensation of Phenyl β -Aminoethyl Ketone with Nitromalonaldehyde. WILLIAM J. HALE and EDGAR C. BRITTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1020—1026).—In continuation of the work of Hale and Hoyt (*A.*, 1916, i, 71) and of Hale and Honan (this vol., i,), the condensation of sodium nitromalonaldehyde with a methylene group activated by the presence of a neighbouring carbonyl group has been studied.

α -Nitro- β -benzoylethylaminoacetaldehyde,



small prisms, m. p. 153°, is readily produced when an aqueous solution of molar quantities of sodium nitromalonaldehyde and phenyl β -aminoethyl ketone hydrochloride is maintained at 50° for some hours. When twice the relative amount of the amino-ketone hydrochloride is used and the solution is treated with a little sodium hydroxide, β -nitro- α -benzoylethylamino- γ -benzoylethyliminopropylene, $\text{COPh} \cdot [\text{CH}_2]_2 \cdot \text{NH} \cdot \text{CH} : \text{C}(\text{NO}_2) \cdot \text{CH} : \text{N} \cdot [\text{CH}_2]_2 \cdot \text{COPh}$, colourless clusters of needles, m. p. 145° (*platinichloride*, m. p. 208°), is produced, which is decomposed by boiling concentrated hydrochloric acid into the nitroacetaldehyde, m. p. 153°, and phenyl β -aminoethyl ketone; the compound can also be obtained by addition of sodium hydroxide to an aqueous solution of the nitroac-

aldehyde. 4-Nitro-3-phenacylpyrrole,
$$\begin{array}{c} \text{C}(\text{NO}_2) = \text{CH} \\ | \\ \text{CH} : \text{C}(\text{CH}_2 \cdot \text{COPh}) \end{array} > \text{NH},$$

is formed by the condensation of phenyl β -aminoethyl ketone hydrochloride and sodium nitromalonaldehyde in aqueous-alcoholic solution in the presence of sodium hydroxide, or from benzoylethylaminonitroacetaldehyde under similar conditions; it forms small,

lemon-yellow prisms, m. p. 170° (the *platinichloride* decomposes above 300° without melting). Attempts to oxidise the substance to a nitropyrrolecarboxylic acid were unsuccessful. The yield of the pyrrole derivative is only moderate, and the alkaline mother liquors from the preparation yield, on acidification, a red, amorphous precipitate, decomposing between 127° and 132° , which appears to consist of 3-nitro-5-amino-1-benzoylcyclopentadiene,

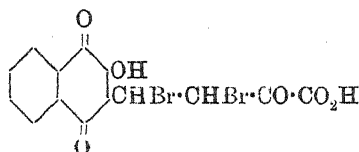
$$\text{COPh}\cdot\text{C}:\text{CH} \begin{array}{l} \text{CH}\cdot\text{NO}_2 \\ \text{NH}_2\cdot\text{C}:\text{CH} \end{array}$$

H. W.

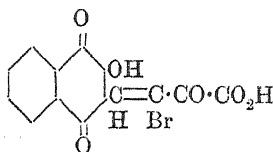
Condensation of Deoxybenzoin and Aldehydes. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (T., 1919, 115, 817--820).

Condensation of Deoxybenzoin with Aromatic Aldehydes. BAWA KARTAR SINGH and JATINDRA KUMAR MAZUMDAR (T., 1919, 115, 821--825).

Action of Potassium Ferricyanide on Alizarin in Alkaline Solution. II. R. SCHOLL and A. ZINKE (Ber., 1919, 52, [B], 1142--1160. Compare this vol., i, 25).—Addition of bromine to hydroxynaphthaquinonylvinyglyoxylic acid leads to the formation of β -[2-hydroxy-1 : 4-naphthaquinonyl-3-vinyglyoxylic 'acid' dibromide (I), m. p. about 150° (decomp.) after softening at about 83° , which slowly loses hydrogen bromide at the ordinary temperature and forms a mixture of cumarinoid (α) (II) and *cumaroid* (β)

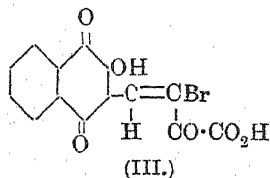


(I.)



(II.)

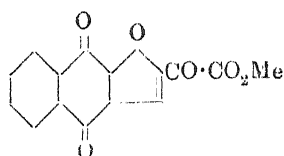
β -[2-hydroxy-1 : 4-naphthaquinonyl-3]- α -bromovinylglyoxylic acids (III), which could not be separated owing to their instability.



(III.)

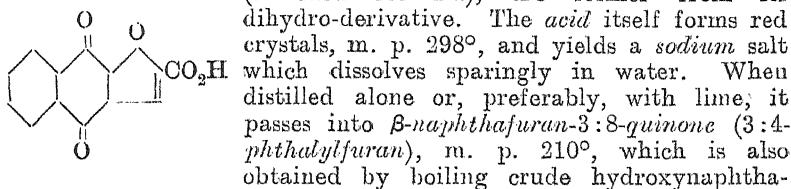
Cumaroid Series.—Methyl β -[2-hydroxy-1 : 4-naphthaquinonyl-3]- α -bromovinylglyoxylate, yellow prisms, m. p. 217° (decomp.), is obtained mixed with methyl naphthafurylquinonylglyoxylate by the action of boiling methyl alcohol on the crude dibromide; the *acetyl* derivative forms pale yellow, shining leaflets, m. p. 188 — 189° . The *ethyl* ester has m. p. 158° . Cautious hydrolysis of the methyl ester yields the corresponding acid, m. p. 171 — 172° (decomp.) after previous darkening and softening, which is transformed by boiling water into naphthafuranquinone (see later). and by boiling xylene into a crystalline acid, m. p. about 251 — 252° . When heated alone at 100° or with alcohol, it is converted into bromobenzocumarinquinone. When

treated with methyl alcohol and hydrogen chloride, it re-forms the methyl ester, m. p. 216—217°. *Methyl β-naphthafuryl-3:8-quinone-1-glyoxylate* (annexed formula)



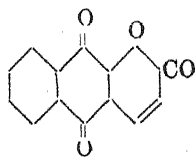
crystallises in reddish-yellow needles, m. p. 222—223°, whilst the corresponding *ethyl* ester forms reddish-yellow needles, m. p. 187° (*phenylhydrazone*, brown needles, m. p. about 208—210°); the latter is oxidised by dilute nitric acid at 200° to phthalic acid. The

esters are converted by methyl-alcoholic potassium hydroxide into a green salt, which is rapidly oxidised by air to a red salt, the latter being derived from naphthafuranquinonecarboxylic acid (annexed formula), the former from its dihydro-derivative. The *acid* itself forms red



crystals, m. p. 298°, and yields a *sodium* salt which dissolves sparingly in water. When distilled alone or, preferably, with lime, it passes into *β-naphthafuran-3:8-quinone* (3:4-*phthalylfuran*), m. p. 210°, which is also obtained by boiling crude hydroxynaphthaquinonylbromovinylglyoxylic acid or pure *β*-hydroxynaphthaquinonyl-*α*-bromovinylglyoxylic acid with water. It yields a *mono-phenylhydrazone*, purple needles, m. p. 158—159°, and a *dibromide*, reddish-yellow crystals, m. p. 112—114° (decomp.), after previous softening, which slowly loses hydrogen bromide at the ordinary temperature. When boiled with glacial acetic acid, the dibromide is converted into a mixture of 1- and 2-*bromonaphthafuranquinones*, yellowish-red leaflets and red needles, m. p. 167—168°, after much softening.

Cumarinoid



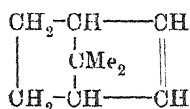
m. p. 224—225°.

2:2-Dibromo-1:3-diketohydrindene, m. p. 175—177°, is obtained by the action of an excess of boiling bromine water on hydroxynaphthaquinonylvinyglyoxylic acid. H. W.

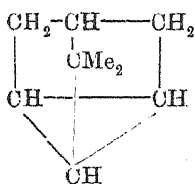
The Basic Properties of Phenanthraquinone. JOSEPH KNOX and HELEN REID WILL (T., 1919, 115, 850—852).

Studies in the Camphane Series. XXXVII. Aryl Derivatives of Imino- and Amino-camphor. MARTIN ONSLOW FORSTER and HANS SPINNER (T., 1919, 115, 889—895).

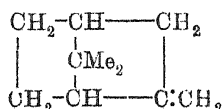
Ozonisation of *apo*Bornylene and of the different Fenchenes. Constitution of these Hydrocarbons. R. H. ROSCHIER (*Acad. Sci. Fennicae*, 1919, [4], 10, 1—83; from *Chem. Zentr.*, 1919, i, 726—730. Compare Komppa and Hentikka, A., 1912, i, 278; 1914, i, 557).—*apo*Bornylene is a mixture of two isomeric hydrocarbons, one of which is the actual *apobornylene* (I), whilst the other is tricyclic *apocyclene* (II). Fenchene is a mixture of at least five terpenes, two of which are semicyclic, two endocyclic, and one tricyclic. Ozonisation of *d*-fenchene (Wallach's *D-l*-fenchene) has confirmed the formula (III) for it, whilst the formula IV may be ascribed with certainty to β -fenchene (Wallach's *D-d*-fenchene and Semmler's *isofenchene*). The fenchene, b. p. 145—147°, is mainly ring-unsaturated, and probably has the constitution (V). The fenchene of lowest boiling point is identical with Semmler's *isoallofenchene* (VI). A small amount of *cyclofenchene* (VII) identical with Aschan's β -pinolene is contained in the fractions of fenchene of lowest boiling point.



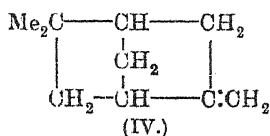
(I.)



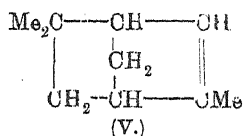
(II.)



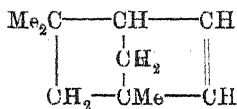
(III.)



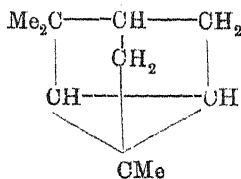
(IV.)



(V.)



(VI.)



(VII.)

*apo*Bornylene was prepared from camphenilole by the xanthate method and from camphenilone through the dichloride; the product obtained by the first method was a completely solid, viscous, camphoraceous mass, m. p. 38°, b. p. 138°/760 mm., whilst that obtained by the second process, b. p. 138—139°, was oily at the ordinary temperature, but solidified when moderately cooled. Attempts to prepare *apobornylene* by the distillation of

camphenilylamine phosphate in a current of carbon dioxide were unsuccessful, the original amine being recovered. Ozonisation of *apobornylene* yielded a normal *ozonide*, $C_9H_{14}O_3$, voluminous, white powder, m. p. 55° (decomp.), which became transformed into a brown oil after some months; it decomposes quietly when heated. Fission of the *ozonide* by warming its solution in acetic acid yielded mainly three fractions; the most volatile was an oil, which did not reduce Fehling's solution, gave no semicarbazone, and probably consisted of *apocyclene acetate*. The middle fraction was aldehydic, but contained some peroxide; it could not be purified by means of a crystalline semicarbazone. The *apobornylenedialdehyde* was so unstable that it became resinified for the most part during distillation, and was converted into *apocamphoric acid* by treatment with potassium carbonate. *apoCamphoric anhydride*, m. p. $174-175^\circ$, was obtained from the least volatile fraction.

When the *ozonide* of *apobornylene* obtained from camphenylene dichloride was decomposed in acetic acid solution and the latter was distilled, the distillate was found to contain *apocyclene* (20—30% of the *apobornylene* taken); the latter is not attacked by ozone, and is extraordinarily stable towards permanganate. It is a readily volatile, crystalline substance with a sweetish, but rather irritating, odour. It has m. p. $42.5-43^\circ$, b. p. $138-139^\circ/764$ mm., D_4^{40} 0.8710, n_D^{40} 1.45144, mol. ref. 37.80 (calc. for tricyclic, C_9H_{14} , 37.16), n_a^{40} 1.44910, n_β^{40} 1.45686, n_γ^{40} 1.46190. *apobornylene*, obtained by the xanthate process, contained 62% of *apocyclene*. Treatment with acetic acid in the presence of sulphuric acid converted *apocyclene* into the acetate, b. p. $81-82^\circ/8$ mm., D_4^{20} 0.9971, n_D^{20} 1.4623, n_a^{20} 1.4601, n_γ^{20} 1.4729. It was hydrolysed to an alcohol, which was not obtained in a state of purity owing to lack of material, but which was identified as β -fenchocamphorol by its oxidation through β -fenchocamphorone to *apofenchocamphoric acid*; the latter could be separated into *trans-apofenchocamphoric acid*, m. p. $144-145^\circ$, and β -fenchocamphorone, m. p. $60-63^\circ$, characterised by its semicarbazone, m. p. $200-201^\circ$.

The α -fenchene was obtained from fenchyl chloride, and had b. p. $155-160^\circ$, $D_4^{17.5}$ 0.8670, $n_D^{17.5}$ 1.46729, α_D^{20} -32.32 . The *ozonide* was a viscous, colourless oil which did not explode when heated, and contained more highly oxygenated products than the normal *ozonide*. After fission, it yielded about 50% of α -fenchocamphorone (identical with Wallach's *D α* -fenchocamphorone), b. p. $198-200^\circ$ (semicarbazone, m. p. $220-221^\circ$). In addition, there were formed a neutral, aldehydic, yellow oil, b. p. $120-133^\circ$, which could not be purified, and α -fenchenylic acid (7 : 7-dimethyl-1 : 2 : 2-bicycloheptane-2-carboxylic acid), m. p. $71.5-72^\circ$. The zinc salt is less soluble in hot than in cold water; the *anilide* forms silky needles, m. p. $149.5-150^\circ$.

The specimen of β -fenchene employed was obtained by distillation of *r*-fenchyl alcohol with potassium or sodium hydrogen sulphate in a current of carbon dioxide. It was separated into

three fractions by repeated distillation, the most volatile of which was purely endocyclic, the least volatile purely semicyclic, according to optical analysis; β -fenchene was contained in the fraction, b. p. 151—153°. β -Fenchene ozonide forms a viscous, syrupy oil which contains more highly oxygenated products than the normal ozonide. Fission yielded impure fenchocamphorone, which was identified by its semicarbazone, m. p. 193—195°; further oxidation of the liquid ketone led to the isolation of a little apocamphoric anhydride (thus proving the presence of α -fenchocamphorone as impurity), and mainly to apofenchocamphoric acid (4:4-dimethylcyclopentane-1:3-dicarboxylic acid), prisms or monoclinic plates, m. p. 144—145°; since the acid cannot be converted into an anhydride in the usual manner, it must be a *trans*-form; the zinc salt, which is less soluble in hot than in cold water, is very characteristic.

The intermediate fraction of the hydrocarbon mixture, b. p. 145—147°, behaved on ozonisation as a compound unsaturated in the ring. It is a mixture of two hydrocarbons, one of which is *isoallofenchene* (VI), whilst the other probably has the constitution V. Fission of the ozonide yielded mainly a *dialdehyde* and a *keto-acid*. The dialdehyde, $C_{10}H_{16}O_2$, is a mobile, yellow oil, b. p. 118—120°/10 mm., D_4^{20} 1.0215, n_D^{20} 1.4700, n_D 1.4677, n_D 1.4815, which is very unstable when exposed to air, and could not be isolated in the pure state; its *disemicarbazone* crystallises in fine granules, m. p. 219°. The crude aldehyde fraction contained also a small quantity of *r-cis-isofenchocamphoric acid*. The keto-acid, $C_{10}H_{16}O_3$, forms a viscous, yellow oil, D_4^{20} 1.0924, n_D^{20} 1.4774, which could not be caused to crystallise, and was purified by means of its *semicarbazone*, m. p. 220—221°; it contains the -COMe group, since, when treated with bromine and alkali, it yields bromoform and a dibasic acid, $C_9H_{14}O_4$, prisms, m. p. 147—148°, which, contrary to expectation, is not identical with apofenchocamphoric acid obtained by the oxidation of β -fenchocamphorone. Full investigation of the acid was impossible owing to the small amount of available material, but its properties show it to be *cis-apofenchocamphoric acid*.

Fission of the ozonide obtained from the most volatile fraction of the β -fenchene hydrocarbon mixture yielded aldehydic and acidic components, together with a small amount of a pleasant-smelling, oily *ketone*, $C_9H_{14}O$ (*semicarbazone*, m. p. 209°), which could be oxidised to an *acid*, probably $C_9H_{14}O_4$. The substances could not, however, be fully investigated owing to lack of material. The acidic fraction contained the keto-acid described above in small amount, together with *r-cis-isofenchocamphoric acid*, m. p. 173—174°, and an aldehydic acid which, on further oxidation, was transformed into *cis-isofenchocamphoric acid*, thus showing the fraction to consist mainly of *isoallofenchene* (VI).

The small portion of this fraction which was not attacked by ozonisation consisted of the hydrocarbon, *cyclofenchene*, $C_{10}H_{16}$, b. p. 142—143°, $D_4^{18.5}$ 0.8624, $n_D^{18.5}$ 1.45364, mol. ref. 42.73. It is

shown to be identical with Aschan's β -pinolene (VII) by its conversion into the hydrochloride, m. p. 26—28°. The *hydrobromide* has m. p. 4°, b. p. 92—93°/12 mm., D_4^{20} 1.2389, n_D^{20} 1.50570, mol. ref. 52.04. Like β -pinolene, it could be converted through the acetate into *isofenchyl* alcohol, *isofenchone*, and *r-isofenchocamphoric* acid.

H. W.

Behaviour of an Alcoholic Solution of Lead Acetate towards the Resinous Substances of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1919, **24**, 95—104, 129—138, 165—173).—The first section of this paper deals with the previously published work of Tschirch ("Die Harz und Harzbehälter," Berlin, 1906). A résumé of the results and conclusions drawn is given, and these are critically discussed. In the third section experiments on the behaviour of the resinous substances of colophony are described. A solution of powdered colophony is made in 5% sodium hydroxide, which on treatment with sodium chloride solution deposits greyish-white needles; the mother liquor, on treatment with hydrochloric acid, gives a precipitate which after washing is practically all soluble in water. On precipitating this solution with a few drops of hydrochloric acid, an acid, m. p. 123°, is precipitated. This is β -*KLw*-resin acid (colophony water soluble resin-acid). The behaviour of the various solutions of colophony with alcoholic solutions of lead acetate is also studied, and it is shown that the starting material in all previous investigations is the colloidal substance γ -pinic acid, m. p. 75—76°. This substance is slowly decomposed by the bound colloidal water in boiling alcoholic solutions. The colloidal behaviour of the components of colophony, particularly in their changes, is probably due to special holding power which resinous substances are able to exert on one another, and thereby an apparent formation of new chemical substances occurs. The residue from the *KL* substances soluble in sodium hydroxide furnishes an example of this type of substance. These extraction residues must not be confused with the decomposition products, which are obtained on washing, through the changes occurring in β -pinic acid, m. p. 98—100°, and those are probably the substances from which fossil resins are produced. Just as the resinous substances often form weak, but well-crystallised, compounds with hydrocarbons by virtue of the holding power mentioned above, so γ -pinic acid forms similar weak compounds with ethereal oils which constitute the turpentine resins. The method used by Tschirch leads to new substances which are not present in the original material. This is particularly the case for a series of amorphous substances of low melting point isolated by Tschirch from recent fossil resins. A method of separation, due to Tschirch, which leads to the acceptance of three abietic acids (α , β , and γ) is to be regarded in the above sense. Although the use of alcoholic lead acetate does not destroy the colloidal condition of the substances treated with it, for example, in the case of γ -pinic acid, yet a change in the so-called colloidal constitution is to be observed. Under the term colloidal constitution the author

understands the method of combination and the number of molecules of colloidal water in the molecule; these are distinguishable by the tannoid properties of the corresponding resin soaps and by the decomposition and associating properties of the free resin acids. Just as γ -pinic acid retains its colloidal water under treatment with lead acetate, so γ -pinic acid in its weak hydrocarbon compounds retains the hydrocarbon when precipitated by the same reagent. True resinous substances are to be distinguished from resin-like substances. The former differ from the latter in their power of passing into crystalline substances, the so-called absolute resins, whereas the latter are not crystallisable. The colophony substance is, in consequence of its colloidal nature, a living substance, which does not come to rest until the colloidal water is used up and thereby a labile equilibrium is set up. The stable condition is probably reached in amber. J. F. S.

The Mutual Influence on the Electrolytic Conductivity of Gallotannic Acid and Boric Acid in Connexion with the Composition of the Tannins. J. BÖESEKEN and W. M. DEERNS (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 907—910).—The researches of E. Fischer have shown that the tannin of the gall nut consists principally of a mixture of the pentadigalloyl ethers of α - and β -glucose, and if this is the case the influence of the conductivity of this substance on that of boric acid should be considerable. Experiments have therefore been performed on the conductivity of solutions of methyl gallate and of the tannin of the gall nut in the presence of boric acid; the increase in conductivity is very considerable and markedly higher in the case of the tannin than in that of the methyl ester, thus agreeing with the presence in the tannin of ten pairs of favourably situated hydroxyl groups in every molecule. H. W.

Tannins. II. Chebulic Acid. KARL FREUDENBERG (*Ber.*, 1919, **52**, [B], 1238—1246).—Chebulic acid is a moderately strong acid in which the presence of a free carboxyl group has previously been assumed, and this hypothesis is now further confirmed. It cannot be hydrolysed by tannase, probably on account of the inhibiting action of the acid group. When heated in aqueous solution, the acidity increases, particularly at first, far more rapidly than is required by the gallic acid eliminated, so that a second, unknown acid appears to be first liberated. This is shown to be the case, since after removal of gallic acid with ether, neutralisation of the solution, and extraction of a crystalline tannin with ethyl acetate, an apparently new, phenolcarboxylic acid can be isolated in the form of its thallium salt; analyses of the latter have not yet yielded absolutely concordant results, but it appears to contain 5—6% of water and to approximate in composition to thallium gallate; it has $[\alpha]_D^{20} + 34^\circ (\pm 4^\circ)$ in water. The crystalline tannin, mentioned above, has $[\alpha]_D^{18} + 85^\circ (\pm 4^\circ)$ in alcoholic solution, and appears to be a digalloyl glucose. Further work on chebulic acid is promised, but the results so far obtained seem to indicate that the

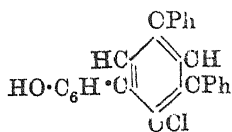
glucose is esterified with two molecules of gallic acid, and that the new acid is not attached to the glucose residue through its carboxyl group, which is free, but probably by a glucosidic linking.

The use of thallium carbonate or hydroxide for the neutralisation of solutions after hydrolysis appears very advantageous, since it can readily be removed by addition of halogen acid, and, in this particular instance, it also effects the precipitation of highly-coloured impurities.

H. W.

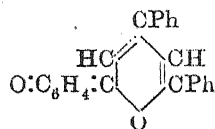
Pyrylium Compounds. IV. Hydroxypyrylium Salts, their Pseudo- and Anhydro-bases. W. DILTHEY (*Ber.*, 1919, 52, [B], 1195—1207).—The previous work (*A.*, 1917, i, 578, 660) has been extended to the anthocyanidines.

Phenyl styryl ketone and *p*-methoxyacetophenone react with ferric chloride in acetic anhydride solution to yield the iron salt, $C_{24}H_{19}O_2Cl_4Fe$, red prisms, m. p. 254—255°, which is converted by sodium carbonate into *α-hydroxy-γε-diphenyl-α-p-anisyl-Δ^α-pentadien-ε-one*, $OMe \cdot C_6H_4 \cdot C(OH) : CH \cdot CPh : CH \cdot CPh$, almost colourless, transparent prisms, m. p. 105—106° (*picrate*, slender, orange needles, m. p. 237—238°), which is slowly



attacked by boiling alcoholic potassium hydroxide solution, yielding anisic acid. Demethylation of the enol is effected by hydrochloric acid at 160°, whereby 2:4-diphenyl-6-*p*-hydroxyphenylpyrylium chloride (annexed formula) is formed in dark yellowish-red prisms, m. p. 293—294°. When a solution of this salt in pyridine

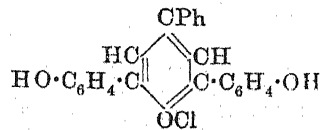
is treated with alcohol and much water, it yields *α-hydroxy-γε-diphenyl-α-p-hydroxyphenyl-Δ^α-pentadien-ε-one*, slender, yellow needles, which darken when heated and have the same m. p. as the *anhydro-base*; the latter (annexed formula) which is best prepared by the action of heat on the enol, forms violet-blue aggregates, m. p. 164°.



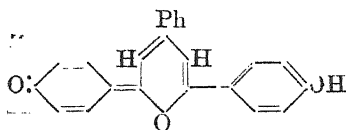
p-Hydroxyphenyl styryl ketone condenses with *p*-hydroxyacetophenone in the presence of zinc chloride and acetic anhydride to yield a complex zinc salt, from which the *platinichloride*, $C_{54}H_{42}O_{10}Cl_6Pt$, microscopic, orange needles, m. p. 258—259°, is obtained by double decomposition; the zinc salt is transformed by sodium acetate into the *diacetyl compound* of the *pseudo-base*,

$OAc \cdot C_6H_4 \cdot C(OH) : CH \cdot CPh : CH \cdot CO \cdot C_6H_4 \cdot OAc$, almost colourless, silky needles, m. p. 122° (*acid picrate*, long, yellow needles, m. p. 232—234°; *perchlorate*, orange-yellow, six-sided platelets, m. p. 249—250°).

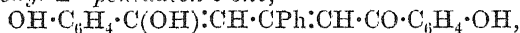
When treated with hot hydrochloric acid, the acetyl groups are removed; the *chloride* of the cyclic base being formed (annexed formula); it forms very stable, orange leaflets ($+ \frac{1}{2}H_2O$), which do not melt below 320°. It may



also be prepared by demethylation of α -hydroxy- γ -phenyl- α -di-*p*-anisyl- Δ^{γ} -pentadien- ϵ -one with hydrochloric acid at 160°. The corresponding perchlorate (+ $\frac{1}{2}$ H₂O) has m. p. 296—298°. The *anhydro*-base (annexed formula), slender needles, decomposing at about 340°, is conveniently prepared by addition of sodium carbonate to a solution of



the perchlorate or *sulphate*, the chloride being too sparingly soluble for this purpose. When a solution of the base in pyridine is cautiously treated with alcohol and water, α -hydroxy- γ -phenyl- α -di-*p*-hydroxyphenyl- Δ^{γ} -pentadien- ϵ -one,



is precipitated in almost colourless, coarse needles which do not show a definite melting point; when heated at 130—140° it is re-converted into the *anhydro*-base.

H. W.

Cryptopine. II. WILLIAM HENRY PERKIN, jun. (T., 1919, 115, 713—790).

A New Method for a Separate Extraction of Hydrastine and Berberine from Golden Seal on a large Scale. ELSA SCHMIDT (*Amer. J. Pharm.*, 1919, 91, 270—275).—Hydrastine is extracted from golden seal by percolation with benzene containing a trace of ammonia, and is isolated by extracting with 3% sulphuric acid and precipitating with ammonia. From the residual drug berberine is extracted by percolation with dilute aqueous acetic acid, and isolated as its hydrochloride by adding hydrochloric acid to the percolate. The author reviews the properties and uses of the two alkaloids, and the methods available for their detection and estimation.

G. F. M.

Action of Hydrogen Peroxide on Sparteine and isoSparteine. AMAND VALEUR and E. LUCE (*Compt. rend.*, 1919, 168, 1276—1278).—Sparteine dioxide, C₁₅H₂₆O₂N₂, obtained by the action of hydrogen peroxide (compare Wackernagel and Wolfenstein, A., 1904, i, 917), is a strong base. Its hydriodide is not decomposed by potassium hydroxide as stated by Ahrens (compare A., 1887, 1056; 1891, 842; 1893, i, 232), but, on the other hand, the base in cold concentrated aqueous solution decomposes potassium iodide. The hydriodide, C₁₅H₂₆O₂N₂·HI, is reduced by hydriodic acid, giving *N*-hydroxysparteine periodide, C₁₅H₂₆N₂(OH)I₂, m. p. 134°, which on further reduction gives a *sparteine periodide*, C₁₅H₂₆N₂·2HI·I₂, m. p. 187°. The *hydriodide of hydroxysparteine iodide*, C₁₅H₂₆N₂(OH)I·HI, has m. p. 256—260°. Sparteine dioxide gives a *methiodide*, C₁₅H₂₆ON₂(OMe)I, m. p. 130°, which on reduction loses its methoxy-group and gives sparteine.

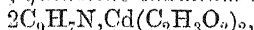
isoSparteine resembles sparteine in its behaviour towards hydrogen peroxide. It yields *isosparteine dioxide*, m. p. 115·5°, a strong

base, which decomposes potassium iodide in concentrated solutions giving an *iodide*, $C_{15}H_{26}ON_2(OH)I \cdot 2H_2O$, m. p. 83° . The corresponding *bromide* has m. p. $107-109.5^\circ$. W. G.

The Constitution of Surinamine. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 20-24).—The author agrees with Goldschmidt (A., 1913, i, 643) that surinamine is *N*-methyltyrosine. He prepared the latter substance by the method of Friedmann and Gutmann (A., 1910, i, 741), and found that no toxic action followed the administration of 0.5 gram to a rabbit or 1 gram daily to a dog.

Surinamine (ratanhine), according to Goldschmidt, is optically active, $[\alpha]_D = -18.6^\circ$. An attempt to resolve the synthetic and inactive compound by the aid of *Penicillium* was unsuccessful. By subjecting the *N*-methyltyrosine to the action of putrefactive organisms a base was formed which was identified as *p*-hydroxyphenylethylmethylamine. J. C. D.

New Additive Compounds of Quinoline with certain Inorganic Salts. JAMES H. WALTON and CHUAN LING LIANG (*J. Amer. Chem. Soc.*, 1919, 41, 1027-1028).—The following compounds were obtained by saturating synthetic quinoline with the requisite salt at 100° , allowing the solution to cool to the temperature of the room, and separating the crystals: *Quinoline silver thiocyanate*, $2C_9H_7N \cdot AgSCN$, small, white crystals; *quinoline mercuric thiocyanate*, $2C_9H_7N \cdot Hg(SCN)_2$, pale yellow crystals; *quinoline mercurous thiocyanate*, $2C_9H_7N \cdot HgSCN$, small, colourless, shining crystals; *quinoline cupric thiocyanate*, $3C_9H_7N \cdot 2Cu(SCN)_2$, small, yellow crystals; *quinoline cuprous thiocyanate*, $2C_9H_7N \cdot CuSCN$, yellow needles; *quinoline zinc acetate*, $C_9H_7N \cdot Zn(C_2H_3O_2)_2$, colourless, crystalline powder; *quinoline cadmium acetate*,



colourless, crystalline powder. Manganese and cobalt acetates are also readily soluble in quinoline, but do not appear to form additive compounds under the experimental conditions used. H. W.

Intermediates used in the Preparation of Photosensitising Dyes. I. Quinoline Bases. L. A. MIKESKA, J. K. STEWART, and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, 11, 456-458).—The parent bases required for the production of the photosensitising dyes, pinaverdol, pinacyanol, and dicyanine are quinoline, 2-methylquinoline, and 2:6- and 2:4-dimethylquinolines. The well-known methods by which these bases may be prepared from aniline or toluidine have been investigated and certain modifications are proposed, which make it possible to work successfully with hundreds of grams of reagents at a time. The chief innovation is that extractions with ether are employed instead of steam distillations. J. C. W.

Intermediates used in the Preparation of Photosensitising Dyes. II. Quaternary Haloids. CARL H. LUND and LOUIS E. WISE (*J. Ind. Eng. Chem.*, 1919, 11, 458-460).—The quinoline

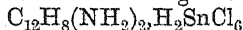
bases mentioned in the preceding abstract are treated with an equimolecular quantity of methyl or ethyl iodide in a round-bottomed flask connected with a reflux condenser, care being taken to modify the reaction by cooling when it has once set in, except in the case of the bases with methyl in position 2, which require prolonged heating on a water-bath. The quaternary iodides obtained by the authors usually melted at the published temperatures, but higher figures are given for 2:6-dimethylquinoline methiodide, m. p. 246—247°, and 2:4-dimethylquinoline ethiodide, m. p. 223—225°.

J. C. W.

Synthesis of Photosensitising Dyes. Pinaverdol and Pinacyanol. LOUIS E. WISE, ELLIOT Q. ADAMS, J. K. STEWART, and CARL H. LUND (*J. Ind. Eng. Chem.*, 1919, **11**, 460—463).—The authors have prepared about fifteen dyes of this type by following the instructions of the original German patents (D.R.-P. 167159 of 1903 and 172118 of 1905). A product which they designate *Pv* 1 is identical with the German pinaverdol or the sensitol-green of the Ilford Co. It is made by slowly adding sodium methoxide solution to a solution of dry quinoline methiodide in boiling methyl alcohol, and allowing to cool slowly. It resembles splinters of brass in appearance, the crystals being monoclinic; $a:b:c = 1.1014:1:1.6053$, $\beta = 88^\circ 20'$. Another product, *Pc IX*, is identical with pinacyanol or sensitol-red. It is obtained by adding a mixture of sodium hydroxide and formalin to a boiling alcoholic solution of quinoline and quinaldine ethiodides, air being first expelled, then diluting somewhat with boiling water and allowing to cool slowly. It crystallises in lustrous, bluish-green needles. There is no real evidence that quinoline ethiodide enters into the reaction at all, and if it is replaced by potassium iodide, a dye, *Pc X*, is formed, although in poor yield, which is very probably identical with *Pc IX*. Like *Pv* 1, *Pc IX* is a quaternary iodide. If transformed into the chloride by reaction with silver chloride in concentrated hydrochloric acid, it gives *Pc XII*, which is more soluble than the iodide. Absorption curves are reproduced in the original.

J. C. W.

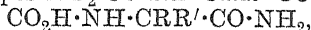
Benzidine Stannichloride. EDWARD BARNES (*Chem. News*, 1919, **119**, 13—14).—In the course of the reduction of azobenzene to benzidine by boiling with stannous chloride in hydrochloric acid, a benzidine stannichloride having the composition



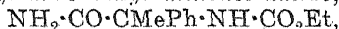
was isolated. The salt forms colourless needles, which are stable in dry air at the ordinary temperature, but evolve hydrochloric acid and stannic chloride when heated to 100°. It is considerably hydrolysed by water or dilute hydrochloric acid, and is only deposited from solution in presence of a large excess of stannic chloride. When mercuric chloride is added to a solution of the benzidine stannichloride, a mercuric salt is precipitated. The composition of the precipitate is indefinite, but by mixing hot solutions of mercuric chloride and benzidine hydrochloride in

equivalent proportions, the salt, $C_{12}H_8(NH_2)_2 \cdot 2HCl, HgCl_2$, is obtained, crystallising in transparent blades, slightly soluble in cold dilute hydrochloric acid, readily in hot. E. H. R.

Preparation of Hydantoins. CHEMISCHE FABRIK VON HEYDEN (D.R.-P. 310427, additional to D.R.-P. 309508 and 310426; from *Chem. Zentr.*, 1919, ii, 423—424. Compare this vol., i, 351).—Substances of the types $NH_2 \cdot CO \cdot NH \cdot CRR' \cdot CO_2H$,



and $NH_2 \cdot CRR' \cdot CO \cdot NH \cdot CO_2H$ ($R = \text{alkyl}$, $R' = \text{aryl}$ or alkyl , with the exception of methyl or ethyl) are treated with a condensing agent, or condensation is effected without an agent by warming in the presence or absence of a solvent or diluent. The sporifics of the main patent are obtained in this manner. *CC*-Dipropylhydantonitrile, $CN \cdot CPr_3 \cdot NH \cdot CO \cdot NH_2$, colourless needles, m. p. 138° , is obtained by converting dipropylketocyanohydrin by means of ammonia into the amino-nitrile, and treating the latter with potassium cyanate in hydrochloric acid solution. It is converted by boiling concentrated hydrochloric acid into *CC*-dipropylhydantoin. A solution of phenylmethylaminoacetoneitrile in hydrochloric acid is converted by potassium cyanate into *phenylmethylhydantonitrile*, colourless needles, m. p. 217° (decomp.), which is further transformed into *phenylmethylhydantoin*, small needles, m. p. 197° . Ethyl *CC*-phenylmethylhydantoate, colourless needles, m. p. 158° , is obtained from ethyl α -amino- α -phenylpropionate hydrochloride and potassium cyanate, and yields *CC*-phenylmethylhydantoin by prolonged boiling with water or by heating alone at 200° . The same substance may also be prepared by the action of potassium hydroxide solution (33%) on *CC*-phenylmethylcarboethylaminoacetamide,



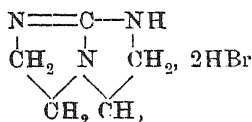
colourless needles, m. p. 191° (from α -amino- α -phenylpropionamide and methyl chloroformate in the presence of sodium carbonate). *CC*-Phenylethylhydantoin is obtained by the action of carbonyl chloride in benzene solution on phenylethylaminoacetamide; carbonyl chloride may be replaced by oxalyl chloride. *CC*-Phenyl-

methylthiohydantoin, $\begin{matrix} Ph \\ | \\ Me \end{matrix} > C < \begin{matrix} CO \cdot NH \\ NH \cdot CS \end{matrix}$, colourless needles, m. p.

169° , is prepared by boiling an alcoholic solution of phenylmethylaminoacetamide with carbon disulphide; if the thiohydantoin is dissolved in boiling sodium hydroxide solution (40%) and the solution diluted with water and again boiled after addition of ferrous sulphate, *CC*-phenylmethylhydantoin is produced. H. W.

Ethyleneguanidine and Diethyleneguanidine. P. PIERRON (*Ann. Chim.*, 1919, [ix], 11, 361—368).—Ethylenediamine in 10% solution and cyanogen bromide, when mixed in equimolecular proportions, readily react to give *ethyleneguanidine hydrobromide*, $\begin{matrix} CH_2 \cdot NH \\ CH_2 \cdot NH \end{matrix} > C \cdot NH, HBr$, m. p. 125 — 126° . From this, by suitable

double decomposition, the *sulphate*, $(C_3H_7N_3)_2H_2SO_4$, m. p. 281° , the *nitrate*, $C_3H_7N_3 \cdot HNO_3$, m. p. 115° , and the *hydrochloride*, m. p. $120-122^\circ$, were obtained. Attempts to isolate the base itself were not successful, but from its aqueous solution, by the action of carbon dioxide, the *carbonate*, $(C_3H_7N_3)_2H_2CO_3$, m. p. 162° , was obtained. Ethyleneguanidine gives metallic derivatives, the *barium*, $C_3H_5N_3Ba$, *lead*, $C_3H_5N_3Pb$, *silver*, $C_3H_6N_3Ag$, and *disilver*, $C_3H_5N_3Ag_2$, derivatives being prepared.



If ethylenediamine is mixed with cyanogen bromide in the molecular proportion of 2:1, or, better still, if ethyleneguanidine hydrobromide is evaporated with an equimolecular proportion of ethylenediamine, *diethyleneguanidine dihydrobromide* (annexed formula), m. p. 224° , is obtained. From this, the *dipicrate*, $C_5H_9N_3 \cdot 2C_6H_3O_7N_3$, m. p. 203° , and the *dinitrate*, $C_5H_9N_3 \cdot 2HNO_3$, m. p. 138° , may be prepared. W. G.

Amphoteric Colloids. V. The Influence of the Valency of Anions on the Physical Properties of Gelatin. JACQUES LOEB (*J. Gen. Physiol.*, 1919, 1, 559-580).—The author has previously suggested a tentative theory to explain the fact that whilst gelatin salts with a univalent cation show a high degree of swelling, viscosity, osmotic pressure, and alcohol number, and gelatin salts with a bivalent metal show, for the same p_H and concentration of gelatin a low degree of swelling, viscosity, osmotic pressure, and alcohol number, yet the conductivities of the two types of salts are practically the same (this vol., i, 296). Curves representing the influence of monobasic acids (hydrochloric, hydrobromic, nitric, and acetic acids) on the osmotic pressure, swelling, and viscosity of gelatin solutions are practically identical, whereas those representing the effect of sulphuric acid are much lower, and stand very much in the same relation to the curves of the monobasic acids as do the curves for calcium gelatinate to those for sodium gelatinate.

The curves representing the influence of other dibasic acids, namely, oxalic, tartaric, succinic, citric, and phosphoric acids, are practically identical with those of the monobasic acids. If the author's theory is correct and it is true that the effect of an electrolyte on the physical properties of the colloid is due to the formation of real chemical compounds between the colloid and one of the ions of the electrolyte it should be possible to prove, first, that twice as many molecules of hydrobromic acid as of sulphuric acid combine with a given mass of gelatin, and secondly, that the same number of molecules of phosphoric, citric, tartaric, oxalic, or succinic acid combine with the same mass of gelatin as of nitric or hydrochloric acid. The present paper gives experimental proof that both these conditions hold.

Gelatin sulphate and gelatin bromide solutions possessing the same p_H have practically the same conductivity. Hence the difference in effect of sulphates and bromides on the physical properties

of gelatin cannot be due to the different ionising and hydration effects of the two acids on the protein molecule. J. C. D.

Pekelharing's Pepsin. V. The Inhibition of the Action of Pepsin by the Bile Acids. W. E. RINGER (*Arch. Néerland. Physiol.*, 1919, 3, 349—360).—The bile acids inhibit the proteolytic action of pepsin. This is not due to a destruction of the enzyme, for if the bile acids are removed by dialysis the proteolytic activity of the pepsin is restored to its original value. The inactivation is probably a result of adsorption phenomena, and the action of the bile acids closely resembles that of certain ions such as the ferrocyanide ion. J. C. D.

Physiological Chemistry.

The Presence of Phosphates in Human Blood-serum. VIII. The Partition of Phosphorus, with Especial Reference to the Phosphorus in Combination with Proteins. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, 94, 293—303. Compare A., 1918, i, 50, 203, 320, 357; this vol., i, 138).—A further study of the distribution of phosphorus in human blood in normal and pathological cases. J. C. D.

The Presence of Phosphate in Human Blood-serum. IX. A Study of Methods and the Distribution of Phosphorus in Normal Erythrocytes. JOH. FEIGL (*Biochem. Zeitsch.*, 1919, 94, 304—312).—The methods and technique are discussed, and figures representing the distribution of phosphorus in the normal red blood cells are given. J. C. D.

Physical Scheme for the Study of the Mineral Nutrition of the Cell. PIERRE GIRARD (*Compt. rend.*, 1919, 168, 1335—1338).—Working on the lines of his previous experiments (compare A., 1908, ii, 456; 1909, ii, 463), the author shows that, in the case of a solution of barium chloride, the barium and chlorine ions will diffuse through a membrane into water, at different proportional rates, according as the solution is acidified with a trace of nitric acid or made alkaline with a trace of ammonia, polarisation occurring at the membrane. These experiments are quoted in further support of his views on the selective permeability of living membranes (*loc. cit.*). W. G.

Enzyme Studies on Cellulose Degradation Products. HANS PRINGSHEIM and ADELHEID MAGNUS VON MARKATZ (*Zeitsch. physiol. Chem.*, 1919, 105, 173—178).—The authors have prepared a cellulose dextrin free from products yielding an osazone reaction

by the method of Madsen (Inaug. Diss., 1917). No evidence of this substance being degraded by the action of diastase could be obtained, nor did emulsin, by virtue of its cellobiase, bring about the formation of any products yielding osazones. Extracts of the first stomach, small intestine, and pancreas of oxen, likewise, had no hydrolytic action, so the conclusion is reached that in the intestinal tract of these animals cellobiose is split by the action of bacteria. Cellobiose is not oxidised to cellobionic acid on boiling with yellow mercuric oxide. J. C. D.

The Stability of Lactalbumin towards Heat. A. D. EMMETT and G. O. LUKOS (*J. Biol. Chem.*, 1919, **38**, 257—265).—The biological value of lactalbumin as a protein for growth did not appear to be diminished by heating at 90—100° in an air oven for sixteen hours, or by treatment in an autoclave at fifteen pounds pressure for two or six hours. There was certainly no evidence that the heated protein was toxic for young rats. The previous conclusions regarding the excellent growth-promoting value of lactalbumin (this vol., i, 363) is further substantiated on the hypothesis that there is a vitamine factor involved which is different from the so-called water-soluble B. J. C. D.

The Nutritive Value of Yeast Protein. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, **38**, 223—227).—Rats were kept for more than a year, covering the period of growth, on a diet in which yeast furnished the sole source of nitrogen, as well as of the water-soluble vitamine. The animals showed a normal rate of growth, but certain cases exhibited sterility on arriving at maturity. This is not attributed to the presence of a toxic factor in the yeast. J. C. D.

The Zinc Content of some Food Products. VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, **38**, 191—203).—The author found the method proposed by Breyer (Scott, "Standard Methods of Chemical Analysis," 1917, 487) satisfactory for the estimation of very small quantities of zinc. Hen's eggs contain about 1 mg. of zinc, of which practically all is present in the yolk. Ordinary market milk contains on an average 4.2 mg. of zinc per kilo, but variations are to be found in the milk from different animals. The zinc content of human milk is markedly higher than that of cow's milk. The presence of zinc both in egg yolk and in milk suggests that this element may exert an important function in nutrition. J. C. D.

The Degradation of Fatty Substances in the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, **105**, 1—19).—The amount of alkali bound after boiling the spinal cord of the frog with *N*/10-sodium hydroxide for two hours may be taken as a measure of the amount of fatty substances present. Using this method of estimation, the authors have shown that the fat content of the surviving cord

gradually diminishes when it is kept in an atmosphere of oxygen or in oxygenated physiological saline solution. The decrease is due to oxidation processes, and is more marked when stimulation is applied. Considerable fat-sparing action may be shown by certain carbohydrates; thus, dextrose may reduce the utilisation of fatty substances some 40% in resting metabolism, and as much as 80% in stimulation. Reasons are given for believing that the substances which bind alkali on hydrolysis, and are utilised during oxidation, are of the nature of phosphatides rather than of true fats.

J. C. D.

The Protein Sugar. HENRI BIERRY (*Compt. rend.*, 1918, 168, 1225—1228. Compare Bierry and Fandard, A., 1914, i, 218, 454, and Bierry and Ranc, A., 1914, i, 346).—If the muscle plays a part in the genesis of protein sugar, differences in the protein sugar content should be found between the arterial plasma and venous plasma from the same group of muscles. This has been shown to be true for the group of muscles of the thigh in the case of the dog. The author suggests that in the muscular protoplasm there exists a complex nitrogenous molecule, the nucleus of which remains invariable, but has attached to its terminal chains peptidic groupings capable of being liberated and then regenerated. These groupings can unite with dextrose and block its aldehyde function.

W. G.

Colours of Colloids. VI. Blue Eyes. WILDER D. BANCROFT (*J. Physical Chem.*, 1919, 23, 356—361. Compare this vol., ii, 275, 324).—In the present paper the colour of blue eyes is discussed. It is shown that there is no pigment on the front of the iris in blue eyes, the blue colour is due to turbid media and is richer the finer the suspended particles. When the uvea is lacking, the colour of the blood shows through and albinism is the result. All other colours in eyes are due to pigmentation on the front of the eye, which either modifies or masks the blue of the turbid media.

J. F. S.

Zinc in Oysters. R. S. HILTNER and H. J. WICHMANN (*J. Biol. Chem.*, 1919, 38, 205—221).—Zinc was invariably found present in the oysters, all of which were grown in Atlantic waters. It is probable that copper is always associated with the zinc. The amount of zinc found could not be correlated with the weight of the system or with the zinc content of the water in which they grew. Considerable quantities of zinc and sometimes traces of copper were detected in the vegetation and organic matter dredged up with the oysters.

It appears probable that zinc and copper can be absorbed by the tissues of the oysters in quantities far in excess of functional requirements.

J. C. D.

Pyrrole and Melanuria. PIETRO SACCARDI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 309—311).—Subcutaneous administration

of pyrrole to a rabbit produces a green coloration of the urine, which afterwards becomes brown. Such urine exhibits no pathological characters, retains its normal alkalinity, and responds to the reactions regarded as characteristic of the melanogens. T. H. P.

Hæmatoporphyrin Congenita. II. O. SCHUMM (*Zeitsch. physiol. Chem.*, 1919, 105, 158—172).—The daily excretion of crude porphyrin in the urine in cases of this disease was found to be fairly constant at various periods during two years. Analyses of crude porphyrin from urine gave higher values for carbon and lower values for hydrogen and nitrogen than were recorded by Fischer (A., 1916, i, 514). The figures for nitrogen are markedly higher than the nitrogen content of free urinoporphyrin, so that it is probable that the crude product is a chemical or physical complex of the pigment with a substance rich in nitrogen. Analyses of purified porphyrin-methyl ester from urine agree with the formula deduced by Fischer, $C_{47}H_{50}O_{16}N_4$. Analyses of the porphyrin methyl ester from faeces agree with Fischer's formula, $C_{39}H_{42}O_8N_4$. The author confirms his previous observation of the occurrence of porphyrin and hæmatin in the blood of patients with this disease, and now finds considerable amounts of bilirubin also. J. C. D.

New Theory relating Constitution to Taste. Simple Relations between the Constitution of Aliphatic Compounds and their Sweet Taste. ERNEST OERTLY and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1919, 41, 855—867).—A preliminary paper, in which a theory of the cause of the taste of sweet substances is put forward. The taste of sweet substances depends on two factors, the presence of a glucophore and an auxogluc. An auxogluc is an atom or radicle which, combined with any glucophore, yields a sweet compound. A glucophore is a group of atoms which has the power to form sweet compounds by uniting with a number of otherwise tasteless atoms or radicles. This theory is considered in the present paper only in connexion with aliphatic compounds. In the sense of the theory the following radicles are glucophores:

(1) $-\text{CO}\cdot\text{CH}(\text{OH})-(+\text{H})$;

(2) $\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)-$; (3) $-\text{CH}_2\cdot\text{O}\cdot\text{NO}_2$; (4) $\text{CH}_2(\text{OH})\cdot\text{CH}(\text{OH})-$;

(5) $\text{C}_{\text{Hal } x}^{\text{H}_2-x}$; (6) $\text{C}_{\text{Hal } x}^{\text{H}_2-x}$, $\text{C}_{\text{Hal } y}^{\text{H}_2-y}$. The following atoms or radicles act as

auxoglucs, forming sweetish compounds with glucophores:

(a) hydrogen, (b) the radicles $\text{C}_n\text{H}_{2n+1}$, containing 1—3 carbon atoms, (c) the radicles $\text{C}_n\text{H}_{2n+1}\cdot\text{O}-$, of the monohydric alcohols, where $n=1$ or 2, (d) the radicles $\text{C}_n\text{H}_{2n-1}\text{O}_n$ of the polyhydric alcohols. A very long list of sweet substances supporting this theory is given. The presence of the phenyl group tends to make

an otherwise sweet compound bitter. Thus ethylene glycol is sweet, but its phenyl derivative is slightly bitter. Some exceptions to the rule are found in stereoisomeric substances; thus *l*-valine, $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, is made up of the glucophore,

$-\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$,

and the auxogluc, CHMe_2 -, and is slightly bitter, but *d*-valine and *dl*-valine are both sweet.

J. F. S.

Is there a Relationship between the Power of Absorbing Radiant Heat and the Odour of Substances? G. GRIJNS (*Arch. Néerl. Physiol.*, 1919, 3, 377—390).—The various attempts which have been made to trace a relationship between the odour of substances and their chemical constitution or physical properties are reviewed. Tyndall ("Heat as a Mode of Motion," London, 1865, 366) observed that gases with an odour possessed the power of absorbing radiant heat to a marked degree. The author has attempted to study this point more fully and quantitatively. An apparatus, termed an odorimeter, devised by Prof. Zwaardemaker for the quantitative measurement of odours is described. No relation between the intensity of the odour and the power of absorbing radiant heat is detected, and it is therefore concluded that the stimulation of the olfactory apparatus is not effected by the liberation of energy absorbed from radiant heat.

J. C. D.

The Biological Action of Thorium. H. JASTROWITZ (*Biochem. Zeitsch.*, 1919, 94, 313—358).—No demonstrable influence of thorium on nuclease or uricolysis was observed. After injections of thorium into dogs, there was a tendency for a higher excretion of uric acid than normally. The fact that thorium may delay the separation of uric acid from its supersaturated solution in serum is held to be of importance from a clinical point of view. The peptolytic enzymes are not influenced by thorium, but the peroxylase is inhibited.

J. C. D.

Genesis of Thiocyanic Acid in Animals. VI. SERAFINO DEZANI (*Arch. Farm. speriment. sci. aff.*, 1918, 26, 115—128; from *Chem. Zentr.*, 1919, i, 485—486. Compare this vol., i, 138).—It has been shown by Bruylants that carbon disulphide is converted into thiocyanic acid by the animal organism. Thiocarbamide appears to be a possible intermediate compound, since its presence in the organism has been detected by Gautrelet. In the case of the rabbit, administration of thiocarbamide did not lead to an increase in the thiocyanic acid in the urine. In the cases of both the rabbit and the dog, elimination of the acid depends greatly on the nature of the nourishment. It is very small when clover is given, but very marked with cauliflower. Its origin with the rabbit is exogenic in nature.

H. W.

Effect of Various Aromatic Substances on the Blood Vessels. Comparison of the Constitution and Action of Drugs. S. KONDO (*Kyoto Igaku Zasshi*, 1917, 14, No. 7, 25—75; *Jap. Med. Literature*, 1919, 4, 18).—The compounds studied were vasodilators, similar in action but differing in degree. They stimulated first the nerve, then the muscle fibre, and vascular paralysis was produced. With few exceptions, if the vasodilator was given

sufficient time to act, the vasoconstrictor action of barium and of adrenaline was prevented. The physiological action of compounds of the aromatic series is due to the benzene nucleus, and is modified by substituents. Monohydric phenols had a more powerful action than either benzene or dihydric or trihydric phenols; a similar relation existed between sodium benzoate and salicylate, and between *cyclohexanol* and *quinitol* (*cyclohexane-1:4-diol*). Of the three isomeric dihydroxybenzenes, *resorcinol* exerted the greatest vasodilator action. *Guaiacol* was more powerful than *catechol*, *phenacetin* than *antifebrin*, *lactophenine* than *aniline*, *phenylhydrazine* than *aniline*. The toxicity was increased by the union of two nuclei. *Naphthalene* was more toxic than benzene, *benzidine* than *aniline*, and *quinoline* than *pyridine*. *Menthol* and *camphor* had an identical action; *pyridine* and *nicotine* acted similarly, likewise *quinoline* and *quinine*. *cycloHexane* was more powerful than benzene, and *piperidine* than *pyridine*. *cyclo-Hexanol* did not exert a more marked action than phenol.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

Biochemical Action of Microbes on Sugars and Alcohols.

A. BESSON, A. RANQUE, and CH. SENEZ (*Compt. rend. soc. biol.*, 1918, **81**, 930—933; from *Chem. Zentr.*, 1919, i, 663—664).—A table is given showing the action of various microbes (*Bacillus faecalis alkaligenes*, *B. pyocyaneus*, *B. Shiga*, *B. Hiss*, *B. Flesner*, *B. typhi*, *Vibrio cholerae*, *B. proteus*, *B. paratyphi A*, *B. paratyphi B.*, *B. coli*) on dextrose, *lævulose*, maltose, *dulcitol*, sucrose, lactose, *mannitol*, and glycerol in the presence of agar or peptone water. The mode of action depends greatly on the form of nutriment, and the manner in which the different sugars and alcohols are attacked does not depend on the nature of the substances, but is a specific property of the respective microbes. The evolution of gas seems to be a more important phenomenon than the fact that a particular sugar is or is not attacked. With regard to their action on sugars and alcohols, microbes may be conveniently classified as follows: (i) inactive microbes which do not attack these substances; (ii) microbes which act without evolving gas; (iii) such as act with evolution of gas. The latter two groups may be subdivided according to the susceptible individual compounds.

H. W.

Benzoic Acid as a Disinfectant. H. P. KAUFMANN (*Zeitsch. angew. Chem.*, 1919, **32**, 199—200).—The bactericidal action of benzoic acid on bouillon cultures of *Staphylococcus* and diphtheria bacilli was investigated, and concentrations as low as 0.08% in the former case and 0.04% in the latter were found to produce

sterility in five days. In steam or water vapour at temperatures as low as 37° , benzoic acid showed a powerful bactericidal action comparable with that of phenol under similar conditions. The volatility of benzoic acid in water vapour from boiling aqueous solutions was determined by passing the vapours through a condenser and estimating the benzoic acid in the distillate. With 1% solutions, the percentage gradually increased from 0.256 at the commencement to 1.088 when 90% of the solution had been distilled off, at which point the remaining acid began to separate as an oil. With 2.5% solutions, the benzoic acid content of the distillate rose from 0.605% initially to 1.006% when 70% had distilled and oil began to separate. With 5% solutions, the corresponding figures were 0.995%, rising to 1.06% when 30% had distilled over. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] G. F. M.

Increase of the Action of Catalase in Yeast Cells. HANS VON EULER and RAGNAR BLIX (*Zeitsch. physiol. Chem.*, 1919, 105, 83—114).—The researches of Phragmén (*Medd. K. Vetenskaps-akad. Nobel-Inst.*, 1919, 5) have shown that fresh yeast can bring about the decomposition of dilute hydrogen peroxide. The decomposition follows, within certain limits, the course of a unimolecular reaction. The reaction constant increases proportionately to the amount of yeast used. The power of decomposing hydrogen peroxide possessed by the living yeast may be increased from two to six times by the addition of small quantities of protoplasmic poisons, such as chloroform, thymol, toluene, and phenol. Analogous cases have been described (Euler and Johansson, *A.*, 1912, i, 807). The catalase action of yeast is also greatly increased by drying at the ordinary temperature, or by dehydration by other means—treatment with alcohol or acetone—provided the enzyme is not destroyed. No appreciable increase in the catalase action of the dried yeast was observed to follow the addition of chloroform or toluene. When emulsions of fresh yeast are maintained at 55 — 63° for from one-half to two hours, there is also a very great increase in the power of decomposing hydrogen peroxide. Such activation is not confined to yeast, but is also found in the case of numerous other organisms.

The catalase action per cell may be raised by treating the yeast with nutritive solutions containing sucrose. The influence of a reducing agent, such as methylene-blue, is to cause an increased activation of catalase, whereas acetaldehyde has an inhibitory action.

The influence of dehydration and of protoplasmic poisons on the enzymes of yeast is discussed, and it is considered not improbable that in the case of catalase they act by preventing or neutralising the action of an inhibitory factor. J. C. D.

Antagonism between Alkaloids and Salts in Relation to Permeability. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 1, 515—519).—It was found that nicotine, caffeine, and cevadine may

antagonise the action of sodium chloride. They decrease permeability, and resemble in this respect salts, such as calcium chloride, which antagonise sodium chloride. J. C. D.

Two Crystalline Salts from the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, 168, 1216—1219. Compare A., 1903, ii, 607, 679, 680).—The author describes methods for preparing two crystalline phospho-organic salts from seeds or from phytin. The first salt is a double sodium calcium salt having the composition $C_6H_{12}O_{27}P_6Ca_2Na_8$, and crystallising in slender needles. The second is a sodium salt, $(C_2H_4O_9P_2Na_4)_3 \cdot 44H_2O$. It crystallises in prisms, and readily yields the corresponding copper and lead salts. W. G.

The Constitution of the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, 169, 37—39. Compare preceding abstract).—The author now inclines to the view that this material is an inositol hexaphosphate which energetically retains 3 mols. of water, and these cannot be removed without decomposing the compound. W. G.

Studies on Enzyme Action. XVII. The Oxydase, Peroxydase, Catalase, and Amylase of Fresh and Dehydrated Vegetables. K. GEORGE FALK, GRACE MCGUIRE, and EUGENIA BLOUNT (*J. Biol. Chem.*, 1919, 38, 229—244).—The oxydase reactions with carrot, yellow or white turnip, potato, and tomato juices are greatly increased on dilution. Apparently some substance, chemically unsaturated, is present which combines with the oxygen, preventing it from acting on the reagent. The peroxydase reaction did not show such increase on dilution. There is no well-defined hydrogen-ion concentration for the maximum action with oxydase, peroxydase, or catalase, but the reactions are, in general, better between p_H7 and p_H10 . They are inhibited by acid reaction, except in the case of the tomato. Vacuum dehydrated cabbage and carrot gave more marked oxydase reactions than did the fresh vegetables, but in every other case the enzyme action was less after dehydration. Well-defined maxima in the amylase reactions are apparent in cabbage, carrot, and turnip juices at about p_H6 . Dehydration causes a decrease in the activity of this enzyme. J. C. D.

A Component of the Fat of *Bassia longifolia* L. (Illipe Malabrorum Kön) and *Bassia latifolia*. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 31—32).—On preserving pieces of the press cake of seeds of *Bassia longifolia* and *B. latifolia* in an evacuated vessel over phosphoric oxide for several months at 30—35°, the surface of the cake became covered with fine, needle-shaped crystals. These were identified as palmitic acid. J. C. D.

The Resin of the Outer Bark of *Melaleuca uncinata*. HENRY G. SMITH (*J. Proc. Roy. Soc. N.S. Wales*, 1917, 51, 232—237).—The thin, paper-like epidermis of the stems and

branches of *Melaleuca uncinata* contains from 20—25% of a resin, which can be extracted with hot alcohol. The resin resembles ordinary shellac in appearance and has D^{15}_D 1.135. About 70% of the total resin is an acid resin, m. p. 148—150°, which gives a potassium and a silver salt. The neutral substances constitute about 25% of the original resin.

In addition to the resin, the outer bark contains a small amount of a vegetable wax, m. p. 67—68°.

W. G.

Isolation of a Saponin from *Platycodon grandiflorum* Root. H. OSHIKA (*Kyoto Igaku Zasshi*, 1918, 15, No. 2, 76—83; *Jap. Med. Literature*, 1919, 4, 20).—The root of the herbaceous plant *Platycodon grandiflorum* (Japanese "Kikyo," Chinese "Kihkang" or "Kihung") is used as an astringent, carminative, sedative, and vermifuge. It contains a saponin, which has the formula $C_{35}H_{48}O_{20}$, is a white powder when pure, is sparingly soluble in water, more readily so in alkali, and is insoluble in acids, ether, and chloroform. Its hæmolytic power is approximately one half that of dioscin. The infusion or decoction of the root has a toxicity for the mouse approximately equal to that of senega root.

CHEMICAL ABSTRACTS.

Composition of Inclusion Cells and their Relation to the Mellowing of Fruits. C. GRIEBEL and A. SCHÄFER (*Zeitsch. Nahr. Genussm.*, 1919, 37, 97—111).—The mesocarp of certain fruits (especially the *Pyrus* species) consists solely of cells containing tannins, and the term "inclusion" cells is given to them, as a distinction from the tannin idioblasts of other fruits and plants. When ripe, fruits having such a mesocarp rapidly become over-ripe or mellow. The single exception, as regards mellowing, is the fruit of *Prunus spinosa* (sloe). The disappearance of the astringent taste during mellowing is not due to decomposition of the tannins, but to their becoming insoluble. The inclusion cells of *Pyrus domestica* contain a tannin which is soluble in water and alcohol; this tannin is, in part, combined with a sparingly soluble colloidal substance of unknown composition; only when the fruit mellowes or is dried do the cell contents become insoluble, brown-coloured substances being formed gradually as this change takes place. Acetaldehyde is formed during the mellowing. The quantity of pentosan and galactan in the inclusion cells of *P. domestica* is very small, and sugars do not appear to be present. The unchanged tannin in the cells yields the reactions of *o*-hydroxy-compounds, an indication that it is a catechol derivative; fusion with potassium hydroxide yields a small quantity of protocatechuic acid, but no phloroglucinol. The tannin possesses no glucosidal character, and its properties resemble those of the oak-bark tannins.

W. P. S.

The Presence of Aconitic Acid in Sugar-cane Juice and a New Reaction for the Detection of the Acid. CHARLES SOMERS TAYLOR (*T.*, 1919, 115, 886—889).

Effect of Manganese Compounds on Soils and Plants.

E. P. DEATRICK (*Cornell Univ. Agric. Exp. Sta. Mem.*, 1919, 19, 371—402).—Manganese salts at high concentrations decrease the growth of wheat in water cultures; at lower concentrations, they stimulate the growth of the plants and increase the oxidising power of the roots. The presence of nutrient salts and the food stored in the endosperm of the wheat seed reduce the toxic effect of the manganese salts. The toxic effect is shown by a browning of the roots and a bleaching of the leaves. The bleached leaves of plants treated with manganese salts contain more manganese than the green leaves. Manganese salts added to the soil increase the power of the soil to oxidise aloin and phenolphthalein. This the author believes is due to the formation of manganese dioxide. Low concentrations of manganese salts stimulate the ammonification of dried blood, but inhibit the nitrification of ammonium sulphate in the soil.

CHEMICAL ABSTRACTS.

Acidimetric Titration of Grain Extracts and Amino-acids in the Presence of Alcohol.

VICTOR BIRCKNER (*J. Biol. Chem.*, 1919, 38, 245—254).—It was found that a larger amount of alkali is required to neutralise the acidity of grain extracts when alcohol is present. A study of this point showed that amino-acids, which in aqueous solution are nearly neutral to phenolphthalein, react distinctly acid in the presence of alcohol. The suggestion is advanced that this may be due to an interaction between the hydrated form of the amino-acid and the alcohol.

J. C. D.

Constituents of Emmenthaler Cheese. V.

E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 25—30. Compare A., 1902, ii, 687; 1904, ii, 585; 1906, ii, 248; 1909, ii, 423).—It has been previously shown that the usual protein cleavage products can be isolated from this cheese, with the one exception of arginine. Arginine was not present in several kinds of skimmed-milk cheese examined. The fate of the arginine has been inquired into. This amino-acid might by ferment action give rise to agmatine, 1:4-diaminobutane, ornithine, urea, and ammonia. 1:4-Diaminobutane was not present, but the presence of urea and ornithine was established. Traces of *p*-hydroxyphenylethylamine were also detected.

J. C. D.

The Statement of Acidity and Alkalinity, with Special Reference to Soils.

EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1919, 9, 305—309).—The author proposes a new method of expressing acidity or alkalinity in place of the usual potential method, in which the value $P_H=7$ indicates neutrality. His scale for chemical potentials is such that $X_H=0$ indicates neutrality, acidity being expressed by positive values and alkalinity by negative. These new values may be arrived at by subtracting the values of P_H from 7.

W. G.

Organic Chemistry.

The Preparation of some True Acetylenic Hydrocarbons by means of Monosodioacetylene. PICON (*Compt. rend.*, 1919, 169, 32—34. Compare this vol., i, 246).—Normal amyl iodide reacts with monosodioacetylene in liquid ammonia, yielding heptinene, together with a small amount of β -methyl- Δ^2 -butene, the latter due probably to the presence of a small amount of active amyl iodide in the sample used.

Normal primary octyl iodide in the same way yields *decinene*, b. p. 59°/13 mm., m. p. -40°, D_4^{20} 0.791, and hexadecyl iodide gives octadecinene, m. p. 22.5°, D_4^{20} 0.8696. W. G.

Carbon Tetrachloride, Chloroform, and Carbon Hexachloride from Natural Gas. G. W. JONES and V. C. ALLISON (*J. Ind. Eng. Chem.*, 1919, 11, 639—643).—Natural gas rich in methane or ethane, such as that of Pittsburgh, can be used for the production of carbon tetrachloride, chloroform, and carbon hexachloride. For this purpose, it is passed, together with a slight excess of chlorine, through a tube which contains a suitable catalyst, and is heated in an electric furnace. The most suitable catalysts are war-gas charcoal, "bachite" (a patent carbon material), and steamed anthracite coal, all of which have a high absorptive capacity for chlorine. The reaction begins at 250° and increases in intensity up to about 500°, above which the catalyst is attacked and carbon is deposited. One litre of natural gas (90% of methane and 10% of ethane) when completely chlorinated should yield 4.01 c.c. of chlorination products. Methane is less readily chlorinated than higher saturated hydrocarbons. By introducing the gas at the rate of 1 litre per hour, methane is completely converted into carbon tetrachloride and ethane into carbon hexachloride. By increasing the rate of introduction of the natural gas, chloroform is obtained in addition to carbon tetrachloride. [See also *J. Soc. Chem. Ind.*, 1919, 599A.] C. A. M.

Preparation of Tetrachloroethylene. H. B. WEISER and G. E. WIGHTMAN (*J. Phys. Chem.*, 1919, 23, 415—439).—The optimum temperature for the thermal decomposition of carbon tetrachloride into chlorine and tetrachloroethylene lies between 1300° and 1400°, but a certain amount of decomposition occurs at temperatures as low as 600°. In order to minimise the further reaction of chlorine on tetrachloroethylene to form solid hexachloroethane, the products of decomposition must be cooled as rapidly as possible, and may with advantage be diluted with an inert gas such as air or nitrogen. The decomposition is conveniently conducted in an electrically heated quartz tube, and an iron condenser may be used provided that the condensing surface

is kept dry and comparatively cool. [See also *J. Soc. Chem. Ind.*, 1919, September.] G. F. M.

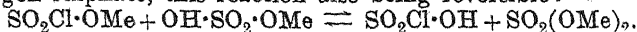
The Catalytic Formation of Alkyl Chlorides from Primary Alcohols. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, 169, 122—125).—When the vapours of primary alcohols of the methyl series are passed along with hydrogen chloride over aluminium oxide at 420°, the corresponding primary alkyl chloride, together with some secondary or tertiary chloride and some ethylenic hydrocarbon, is obtained. In this way, propyl alcohol gives a mixture of propyl and isopropyl chlorides, the latter predominating; isobutyl alcohol gives a mixture of isobutyl chloride, $\text{CHMe}_2\cdot\text{CH}_2\text{Cl}$, and the tertiary chloride, CMe_3Cl , in the proportion of 1:3; isoamyl alcohol gives a mixture of the primary, secondary, and tertiary chlorides in the proportion of 1:2:3, and heptyl alcohol gives heptene and a mixture of primary and secondary heptyl chlorides, together with a little diheptene.

W. G.

The Spontaneous Oxidation of Organic Complexes of Cobalt. H. COLIN and O. LIÉVIN (*Compt. rend.*, 1919, 169, 188—190).—Alkaline solutions of certain organic substances in the presence of cobalt sulphate undergo spontaneous oxidation in the air. In some cases, the amount of oxidation is limited, whilst in others it increases with the time. Glycerol and lactic acid furnish examples of the first type, whilst dextrose, mannitol, erythritol, and tartaric acid are examples of the second class of organic substances. As explanation of this phenomenon, the authors suggest that the cobalt, in the presence of alkali, forms true complexes with the organic compounds. These complexes oxidise spontaneously and turn green, the organic substance being attacked at the same time. If the products of this secondary oxidation are capable of reducing the green complex, there is a continuous transportation of oxygen, but if not the absorption is limited.

W. G.

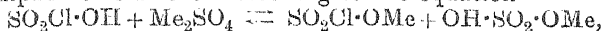
Action of Chlorosulphonic Acid on Methyl Hydrogen Sulphate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, 169, 140—143).—Methyl hydrogen sulphate reacts with chlorosulphonic acid to give methyl chlorosulphonate according to the equation $\text{OH}\cdot\text{SO}_2\text{Cl} + \text{OH}\cdot\text{SO}_2\cdot\text{OMe} \rightleftharpoons \text{SO}_2\text{Cl}\cdot\text{OMe} + \text{H}_2\text{SO}_4$. This reaction is, however, reversible, and an equilibrium is set up. At the same time, a secondary reaction proceeds between some of the methyl chlorosulphonate formed and some of the unchanged methyl hydrogen sulphate, this reaction also being reversible:



As a result of the balance of these reactions, it is found that the yield of methyl chlorosulphonate is only about half of the theoretical yield. Methyl chlorosulphonate is a colourless liquid and a violent lachrymator. It has b. p. 42°/16 mm., 134—135°/760 mm., D_0^{20} 1.514, D_{15}^{20} 1.492, n_D^{20} 1.414.

W. G.

Action of Chlorosulphonic Acid on Methyl Sulphate. Preparation of Methyl Chlorosulphonate. R. LEVAILLANT and L.-J. SIMON (*Compt. rend.*, 1919, 169, 234—236. Compare preceding abstract).—When heated together, methyl sulphate and chlorosulphonic acid react according to the equation



which is, however, reversible. Further, the methyl hydrogen sulphate formed, in its turn, reacts with the chlorosulphonic acid, as already seen. The yield from methyl sulphate is 70% of theory, and may be increased if the product is fractionally distilled, giving two fractions, *A*, containing methyl chlorosulphonate and a little chlorosulphonic acid, and *B*, containing chlorosulphonic acid, methyl chlorosulphonate, and methyl sulphate, this second fraction *B* being added to further quantities of the original reacting mixture.

W. G.

Preparation of the Fluorides of Organic Acids by means of Fluorosulphonic Acid and Fluorosulphonates. WILHELM TRAUBE and ANNA KRAHMER (*Ber.*, 1919, 52, [B], 1293—1298).—The preparation of aliphatic acid chlorides by the action of heat on mixtures of salts of chlorosulphonic acid and fatty acids has been described by the Badische Anilin- & Soda-Fabrik (D.R.-P. 146690); the authors have attempted to prepare the fluorides by a similar method, but the results are not completely satisfactory. The best yields, obtained with fatty aromatic acids, do not exceed 20% of that theoretically possible, whilst with the simple aliphatic acids the yields fall as low as 5%. The by-products include considerable amounts of acid anhydrides. Better results are obtained by heating mixtures of fluorosulphonic acid and the fatty acid in a platinum vessel. The following substances are described: *β*-phenylpropionyl fluoride, b. p. 96°/17 mm., which is only slowly decomposed by water; phenylacetyl fluoride, b. p. 88—89°/17 mm.; benzoyl fluoride, b. p. 156°; acetyl fluoride, b. p. 20·5°; propionyl fluoride, b. p. 44°; chloroacetyl fluoride, b. p. 74°; dichloroacetyl fluoride, b. p. 71—72°.

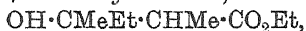
H. W.

Certain Aliphatic Compounds with Numerous Side-chains. RICHARD WILLSTÄTTER and DANIEL HATT (*Annalen*, 1919, 418, 148—160).—The authors have synthesised $\alpha\beta\gamma\delta$ -tetramethylhexoic acid by way of the ester of the corresponding β -hydroxy-acid, the method employed consisting in union of a ketone and the ester of an α -halogenated aliphatic acid in presence of zinc (compare Reformatsky, A., 1887, 717; 1896, i, 128) or magnesium (compare Zelinsky and Gutt, A., 1902, i, 585). The synthesis in this way of ethyl β -hydroxy- $\alpha\beta$ -dimethylvalerate from methyl ethyl ketone and ethyl α -iodopropionate occurs readily, but ethyl isobutyl ketone and ethyl α -iodopropionate yield, in addition to the ester of the β -hydroxy-acid, also that of the corresponding unsaturated acid. Hydrogenation of the latter in presence of platinum gives the $\alpha\beta\gamma\delta$ -tetramethylhexoic acid, which in habit resembles phytol derivatives, without, however, being identical with

any of these. The β -hydroxy-acid is converted by the action of 62%, or even more dilute, sulphuric acid into the highly stable γ -lactone, this behaviour being that exhibited by other alkylated $\alpha\beta$ -unsaturated acids.

$\beta\gamma$ -Dimethyl- δ -pentanone, obtained by boiling ethyl methylisopropylacetoacetate (compare van Romburgh, A., 1887, 232) with hydrobromic and glacial acetic acids, has b. p. 128—133.5°/719 mm. (van Romburgh gave 135—140°); its *oxime*, $C_{17}H_{15}ON$, is a colourless, viscous oil, b. p. 82—82.5°/10 mm., with an odour of peppermint. By sodium and alcohol, the ketone is reduced to $\beta\gamma$ -dimethyl- δ -pentanol, $C_7H_{16}O$, which is a somewhat viscous liquid, b. p. 149—150.5°/719 mm., D_4^{21} 0.836. δ -Iodo- $\beta\gamma$ -dimethylpentane, $C_7H_{15}I$, has b. p. 56—61°/11 mm., and smells like camphor.

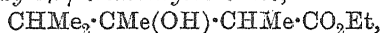
Ethyl β -hydroxy- $\alpha\beta$ -dimethylvalerate,



prepared from methyl ethyl ketone and ethyl α -iodopropionate in presence of magnesium, is a liquid, b. p. 78—79.5°/10 mm.

Ethyl $\alpha\beta$ -dimethyl- Δ^2 -butenoate, $CMeEt \cdot CMe \cdot CO_2Et$, prepared by heating the preceding ester with oxalic acid, is a mobile liquid, b. p. 64—66°/13.5 mm., D_4^0 0.927, with a pleasant odour and a vigorous reducing action on permanganate.

Ethyl β -hydroxy- $\alpha\beta\gamma$ -trimethylvalerate,



prepared from methyl isopropyl ketone and ethyl α -iodopropionate, is a mobile liquid, b. p. 90—93.5°/11.5 mm., $D_4^{17.5}$ 0.977; it is not converted into the corresponding unsaturated ester by either oxalic acid, phosphoric oxide, or phthalic anhydride. The free *hydroxy-acid*, $C_8H_{16}O_3$, forms a viscous liquid, b. p. 136—140°/9.5 mm., and in a desiccator, or more rapidly on heating with dilute sulphuric acid (1:1), is converted into $\alpha\beta\gamma$ -trimethyl- δ -valerolactone, $CHMe \begin{smallmatrix} CMe_2-O \\ \diagup \quad \diagdown \\ CHMe \end{smallmatrix} CO$, which crystallises in needles and

lanceolate leaflets, m. p. 47.5°, b. p. 90.5—93°/10 mm., and has an intense menthol odour. When heated with hydriodic acid and phosphorus, the lactone gives an *alphyll iodide* (? octyl iodide), b. p. 164—167.5°, and a very stable *carboxylic acid* of high molecular weight, b. p. 272—279°/10 mm. When heated for a day at 160—210° with hydriodic acid (D 1.96), the lactone loses carbon dioxide and yields a saturated *hydrocarbon*, b. p. 84—89°, which smells like petroleum and appears to have the composition of a cycloparaffin.

$\alpha\beta\gamma\delta$ -Tetramethyl- γ -hexolactone, $CHMe \begin{smallmatrix} CMePr^{\beta} \cdot O \\ \diagup \quad \diagdown \\ CHMe \end{smallmatrix} CO$, is a some-

what viscous oil, b. p. 117—120°/12 mm., D_4^0 0.988, with an odour like that of menthol, and is only slowly oxidised by permanganate.

Tetramethyl- Δ^2 -hexenoic acid, $CHMe_2 \cdot CHMe \cdot CMe \cdot CMe \cdot CO_2H$, cannot be distilled even in a vacuum, owing to its ready conversion into the lactone, which forms slowly even at the ordinary tempera-

ture; the acid instantaneously combines with bromine and decolorises permanganate.

$\alpha\beta\gamma\delta$ -Tetramethylhexoic acid, $\text{CH}_3\cdot[\text{CHMe}]_4\cdot\text{CO}_2\text{H}$, is a somewhat viscous, colourless oil, b. p. $136\text{--}136\cdot5^\circ/11\text{ mm.}$, $\text{D}_4^{20\cdot5} 0\cdot935$, and smells faintly like turpentine. Its silver salt was analysed.

T. H. P.

Transformation of Acid Salts of Dibasic Acids in Aqueous Solution. TH. SABALITSCHKA (*Ber.*, 1919, 52, [B], 1378—1384).—Previous experiments by Thoms and Sabalitschka (*A.*, 1917, i, 700) have shown that only minute traces of oxalic acid can be removed from aqueous solutions of potassium hydrogen oxalate by treatment with ether, this behaviour being in striking contrast with that observed with the acid salts of other dibasic organic acids. The author has therefore investigated the dialysis of solutions of potassium hydrogen oxalate of differing concentration and at differing temperatures. It is found that the diffusate invariably contains slightly more potassium in relationship to oxalic acid than is required for the acid salt, whilst the diffusing solution contains an excess of oxalic acid. It appeared probable that this is due to the existence of normal potassium oxalate and potassium tetroxalate in solutions of the hydrogen oxalate, and direct experimental evidence on this point is afforded by the crystallisation of potassium tetroxalate in the pure state from a not too concentrated solution of potassium hydrogen oxalate at $+10^\circ$. Solutions of ammonium hydrogen oxalate do not appear to behave in a similar manner.

It is pointed out that oxalic acid can be completely volatilised at the temperature of the boiling-water bath, and, further, that commercial potassium hydrogen oxalate does not generally correspond with the formula KHC_2O_4 .

H. W.

The Synthesis of Inositol Hexaphosphate and its Identity with the Phospho-organic Reserve Principle of Green Plants. S. POSTERNAK (*Compt. rend.*, 1919, 169, 138—140. Compare this vol., i, 426).—Inositol hexaphosphate has been synthesised and isolated in the form of its double calcium sodium salt by heating inositol with phosphoric acid in the presence of phosphoric oxide at $120\text{--}130^\circ$ for three hours. The crystallographic properties of this synthetic double salt have been examined, and on comparison with those of the double salt prepared from phytin, the two sets of measurements were found to be identical. The crystals are monoclinic [$a:b:c = 0\cdot630066:1:0\cdot639015$ and $\beta = 108^\circ 13'$]. This is taken as conclusive proof that the phospho-organic reserve principle of green plants is inositol hexaphosphate.

W. G.

Improvements Relating to the Preparation of Amines. WILLIAM RINTOUL, JOHN THOMAS, and NOBEL'S EXPLOSIVES CO., LTD. (*Brit. Pat.*, 128372).—Secondary and tertiary amines

are separated from mixtures of the two containing an excess of the latter by treatment with carbonyl chloride at temperatures below 25° , whereby the secondary amine is converted into a carbamide chloride with the elimination of hydrogen chloride, which reacts, forming the hydrochloride of the tertiary amine. The reaction mixture is then treated with sufficient dilute hydrochloric acid to dissolve the whole of the tertiary amine, whilst the insoluble carbamide chloride is collected and boiled with either water or dilute hydrochloric acid to regenerate the secondary amine. In cases where the mixture of amines contains an excess of the secondary amine, the requisite excess of tertiary base is secured either by removing the secondary base in stages by repeating the above operation, or by actually adding a sufficient quantity of tertiary amine to the original mixture. [See, further, *J. Soc. Chem. Ind.*, 1919, September.] G. F. M.

Preparation of Aminosulphonic Acids by the Aid of Salts of Fluorosulphonic Acid. WILHELM TRAUBE and ELISABETH BREHMER (*Ber.*, 1919, 52, [B], 1284—1293).—The salts of fluorosulphonic acid possess the remarkable property of exchanging the fluorine atom for an amino-group when treated with an aqueous solution of the requisite base; under these conditions, a portion of the fluorosulphonic acid, greater or less according to the strength of the base, is hydrolysed to hydrofluoric and sulphuric acids, which represent the sole by-products of the change and which can readily be removed by chalk or barium hydroxide. The process has the considerable advantage over the older methods that it does not require the isolation of the base in the anhydrous condition. The following substances have been prepared in this manner: aminosulphonic acid, aminoethylaminosulphonic acid, barium hydrazinosulphonate, *potassium hydrazinosulphonate*, and *potassium methylaminosulphonate*, shining leaflets. *Methylaminosulphonic acid* forms long needles, m. p. 181° , and yields hygroscopic ammonium and sodium salts; the barium salt ($+H_2O$) is stable in air; the silver, copper, and lead salts are freely soluble in water. The action of potassium nitrite on an aqueous solution of methylaminosulphonic acid leads to the formation of *potassium methylnitrosoaminosulphonate*, $NO \cdot NMe \cdot SO_3K$, which, when reduced with zinc dust and acetic acid, and subsequently boiled with hydrochloric acid, gives methylhydrazine in 18% yield. Potassium ethylaminosulphonate is formed from potassium fluorosulphonate and ethylamine; the corresponding free acid forms clusters of needles, m. p. 167 — 168° . *Propylaminosulphonic acid*, *isobutylaminosulphonic acid*, and *isopropylaminosulphonic acid* are similarly prepared, and have m. p.'s 172 — 173° , 192° (decomp.), and 188° respectively; the potassium salts are described. Phenylaminosulphonic acid is obtained in 38% yield. *Sodium methylhydrazinosulphonate* closely resembles the corresponding ethyl compound; it could not, however, be transformed into the diazomethanesulphonate by oxidation with mercuric oxide. H. W.

α -Amino-alcohols with Secondary Alcohol Function. ERNEST FOURNEAU and (MME.) PAULINE RAMART-LUCAS (*Bull. Soc. chim.*, 1919, [iv], **25**, 364—370).—Chloropropaldehyde readily reacts with magnesium alkyl bromides or iodides to give the corresponding secondary α -chloro-alcohols. These secondary alcohols condense with amines, such as dimethylamine, to give the α -amino-alcohols. The following compounds have been prepared.

α -Chloropentan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$, b. p. 83—85°/20 mm., 100°/60 mm., 173°/760 mm., giving an *acetyl* derivative, b. p. 89°/15 mm., and a *benzoyl* derivative, b. p. 168°/15 mm. α -Iodopentan- γ -ol, b. p. 105—108°/15 mm., is obtained from the chloro-alcohol by the action of sodium iodide. With dimethylamine, α -chloropentan- γ -ol yields α -dimethylaminopentan- γ -ol, b. p. 175°/760 mm., 97°/46 mm. It gives a *hydrochloride* of its *benzoyl ether*, m. p. 120—121°, and a *hydrochloride* of its *p-nitrobenzoyl ether*, m. p. 145—146°. α -Diethylaminopentan- γ -ol has b. p. 76°/13 mm., and yields the *hydrochloride* of its *benzoyl ether*, m. p. 106—107°, and the *hydrochloride* of its *methylcinnamyl ether*, m. p. 136°.

α -Chlorobutan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$, b. p. 70°/13 mm., gives α -dimethylaminobutan- γ -ol, b. p. 150°/760 mm., yielding the *hydrochloride* of its *benzoyl ether*, b. p. 133—134°. α -Diethylaminobutan- γ -ol has b. p. 72°/13 mm.

α -Chlorohexan- γ -ol, $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{CHPr}\cdot\text{OH}$, b. p. 90—91°/13 mm., 120°/35 mm., yields α -dimethylaminohexan- γ -ol, b. p. 193—194°/760 mm., giving the *hydrochloride* of its *cinnamyl ether*, m. p. 134—135°.

α -Chloro- ζ -methylheptan- γ -ol, b. p. 110—115°/13 mm., 128—130°/25 mm., gives α -dimethylamino- ζ -methylheptan- γ -ol, b. p. 120°/28 mm., yielding the *hydrochloride* of its *benzoyl ether*, m. p. 133—134°.

These chloro-alcohols, unlike those obtained from chloroacetone, are obtained quite pure and are very stable to light. W. G.

Carbamylglycollic Acids. ALFRED AHLQVIST (*J. pr. Chem.*, 1919, [ii], **99**, 45—84).—With carbamic acid, hydroxy-acids yield carbamates, for instance, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{NH}_2$, which are at the same time acids and urethanes, and are most suitably named carbamic ester acids, the term urethane acids being better applied to acids of the type $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{R}$. Few of these carbamic ester acids being known (compare Thiele and Dent, A., 1899, i, 14; Lambling, A., 1898, i, 588; 1899, i, 52, 84; 1902, i, 537, 603, 756), the author has made a more extended investigation of them. Oxidation of the corresponding thiocarbamyl compounds by means of bromine or permanganate affords a convenient general method for the synthesis of these acids (compare Holmberg, A., 1905, i, 324; 1907, i, 384; 1910, i, 834; 1912, i, 131), and the author has studied the methods of preparing the thiocarbamylglycollic acids necessary for this synthesis.

Acetaminocarbothiolonglycollic [monoamide of xanthodiacetic]

acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, prepared as sodium salt according to the scheme $\text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{OH} + \text{CS}_2 + \text{KOH} = \text{H}_2\text{O} + \text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{SK}$, and this
 $+ \text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2 \rightarrow \text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CS}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$,
 crystallises in faint yellow prisms and sinters at 123° , m. p. (not sharp) $129\text{--}130^\circ$.

Trithiocarbodiglycollamide, $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, formed during the above synthesis by the action of chloroacetamide on trithiocarbonate derived from the carbon disulphide and alkali, crystallises in golden spangles, m. p. $206\text{--}207^\circ$ (decomp.) or 198° (slow heating).

Thiocarbamylglycollic acid is formed in best yield from ethylcarbothiolonglycollic acid (compare Holmberg, A., 1907, i, 384), but is more readily obtained pure, as ammonium salt, by the action of ammonia (3 mols.) on the monoamide of xanthodiacetic acid (1 mol.). The ammonium salt forms white needles, m. p. about 160° (decomp.). The free acid shows m. p. 125° , or, with rapid heating, $134\text{--}135^\circ$, the varying values being caused by conversion of the acid to a greater or less extent into the anhydride; the temperature, $111\text{--}112^\circ$, given by Holmberg as the melting point of the acid is really that of the anhydride (see below). The ammonium salt formed in the above way is accompanied by dithioglycollamide, $\text{S}_2(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, m. p. $157\cdot5\text{--}158\cdot5^\circ$ (Clæsson, A., 1881, 580, gave m. p. 155°), which results from the oxidation in the air of thioglycollamide (compare Klason and Carlson, A., 1906, i, 232), this being also a product of the decomposition of the monoamide of xanthodiacetic acid by ammonia.

The action of ammonia on carbothiolondiglycollic acid yields, besides the ammonium salt of thiocarbamylglycollic acid, also that of trithiocarbodiglycollic acid, $\text{CS}(\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, m. p. $172\text{--}173^\circ$ (compare Holmberg, A., 1905, i, 324).

Thiocarbamylglycollic anhydride [4-keto-2-thionoxazolidine], $\text{O} \begin{array}{l} \text{CH}_2\cdot\text{CO} \\ \diagdown \quad \diagup \\ \text{CS}\text{--}\text{NH} \end{array}$, forms a woolly mass of soft, hair-like crystals, m. p. $111\text{--}112^\circ$, and is not converted into the corresponding acid on dissolution in water. The compound, m. p. 143° , obtained by heating thiocarbamylglycollic acid with acetic anhydride, and described by Holmberg (A., 1909, i, 286; 1912, i, 130) as this anhydride, consists of carbamylglycollic acid. In virtue of its iminic hydrogen, the anhydride exhibits acid characters, and may be determined titrimetrically.

Ethylthiocarbamylglycollic anhydride [4-keto-2-thion-3-ethyl-oxazolidine] (compare Holmberg, A., 1912, i, 131), prepared by the action of ethylamine on either carbothiolondiglycollic acid or the monoamide of xanthodiacetic acid, forms crystals, m. p. $40\text{--}40\cdot5^\circ$, and is accompanied by thioglycollic acid, b. p. $107\text{--}108^\circ/16\text{ mm.}$ When converted by alkali into a salt of the corresponding acid and oxidised by means of bromine, it yields ethylcarbamylglycollic acid, m. p. $87\text{--}88^\circ$.

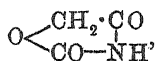
Diethylthiocarbamylglycollic acid, crystals, m. p. $90\cdot5\text{--}91^\circ$, is

obtained by the action of diethylamine on either ethylcarbothiolonglycollic acid or carbothiolonglycollic acid or its mono-amide; the product obtained from the last two acids crystallises well and is accompanied by thioglycollic acid.

In preparing carbamylglycollic acids from the corresponding thiocarbamylglycollic acids, the best oxidising agent is bromine, the action of permanganate resulting in poor yields and often in impure products.

Carbamylglycollic acid thus obtained melts at temperatures varying from 155° to 161° , according to the rapidity of heating, the acid undergoing more profound change than mere conversion into anhydride. The potassium, barium ($+H_2O$), and silver salts, and the ethyl ester, m. p. $64-65^{\circ}$ (Thiele and Dent, *loc. cit.*, give 61°), were prepared. When heated in aqueous solution, the acid decomposes into glycollic acid, carbon dioxide, and ammonia.

Carbamylglycollic anhydride (2:4-diketo-oxazolidine),



m. p. $89-90^{\circ}$, cannot be obtained by heating the corresponding acid, but may be prepared by oxidation of thiocarbamylglycollic anhydride by means of bromine (compare Traube and Ascher, A., 1913, i, 901). It exhibits acid properties, and when titrated with barium hydroxide solution gives a sharp colour change with phenolphthalein. When heated in aqueous solution or in presence of acid, the anhydride undergoes no appreciable decomposition, and the ammonia evolved on distillation with concentrated alkali hydroxide is less than the calculated quantity.

Ethylcarbamylglycollic acid, prepared from ethylthiocarbamylglycollic anhydride by the action of bromine or permanganate in potassium hydroxide solution, has m. p. $87-88^{\circ}$ (Holmberg, A., 1912, i, 131, gave $85-86^{\circ}$). The potassium, barium ($+H_2O$), and silver salts, the *ethyl* ester, $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NH} \cdot \text{Et}$, m. p. $46-47^{\circ}$, and the *amide*, $\text{C}_5\text{H}_{10}\text{O}_3\text{N}_2$, m. p. $120.5-121.5^{\circ}$, were prepared. When heated in aqueous solution or in presence of acid, the acid decomposes, with formation of glycollic acid, carbon dioxide, and ethylamine; with concentrated alkali hydroxide, the decomposition is quantitative.

Ethylcarbamylglycollic anhydride [2:4-diketo-3-ethylloxazolidine], $\text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CO-NEt}' \end{array}$ forms a colourless oil with a characteristic odour,

b. p. $119.5^{\circ}/12 \text{ mm.}$, D_4^{20} 1.246, n_D^{18} 1.462. By cold barium hydroxide solution, it is decomposed, apparently, into glycollethylamide, $\text{NH} \cdot \text{Et} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH}$, but when heated in aqueous or acid solution it remains almost entirely undecomposed. The methylene group of the anhydride does not react with benzaldehyde in presence of acetic anhydride in the same way as that of ethyl- and phenyl-thiocarbamylglycollic anhydrides (compare Holmberg, A., 1912, i, 133), the only separable product of the reaction being benzylidene acetate.

Diethylcarbamylglycollic acid, $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{O} \cdot \text{CO} \cdot \text{NEt}_2$, prepared

by the action of either bromine in alkaline solution or permanganate on diethylthiocarbamylglycollic acid, forms colourless needles, m. p. 77·5—79°; the *potassium*, *barium*, and *silver* salts are described. The *ethyl* ester, $C_9H_{17}O_4N$, is a mobile liquid with a characteristic, fruity odour, b. p. 122—123°/10 mm., D_4^{20} 1·059 n_D^{17} 1·433. Attempts to prepare the amide of the acid resulted in the formation of an uncrystallisable, viscous product, which was not analysed. When heated in aqueous solution or in neutral, acid, or alkaline solution, the acid decomposes into glycollic acid, carbon dioxide, and amine.

T. H. P.

Electrolytic Reaction of Organic Sulphur Compounds.

I. Thioamide Group. MOTOOKI MATSUI and EITARO ASHIDA (*J. Tokyo Chem. Soc.*, 1919, **40**, 147—156).—A compound like carbamide, containing the carbamyl group, is known to react as an imino-compound. According to Werner, the iminocarbamic acid formula expresses the true nature of carbamide. Matsui previously showed (*ibid.*, **30**, 1157) that thioamide groups must be represented by the imino-formula, $RC(NH)SH$. As a further proof for this contention, he and Ashida argue that if the thioamide group acts as an imino-acid, then electrolytic oxidation ought to produce a double sulphur compound, containing two groups of $>C(NH)$ and $-SC(NH)-$. Experimental results seem to confirm their hypothesis. To 1·32 grams of thiocarbamide in 106 c.c. of alcohol are added 4 c.c. of nitric acid (D 1·22). After passing a current of 0·3 to 0·4 ampere for five hours, there appears at the positive platinum pole a white, needle-shaped compound, yielding 1·06 grams after repeated purifications. Analysis shows it to be dithioformamidine dinitrate, $[SC(NH)NH_2]_2 \cdot 2HNO_3$. From acetylthiocarbamide they obtained dithiomonoacetylformamidine. From monophenylthiocarbamide, $H_2N \cdot C(NPh) \cdot S \cdot S \cdot C(NH)NH_2$, is obtained. Thiobenzamide in alcohol is known to be oxidised by iodine to 3:5-diphenyl-1:2:4-thiadiazole. By electrolytic oxidation, they obtained the identical compound, namely, $S < \begin{smallmatrix} N \\ \parallel \\ CPh \end{smallmatrix} = \begin{smallmatrix} N \\ \parallel \\ CPh \end{smallmatrix}$, m. p. 90°, instead of the dithio-compound. In the same way, thioacetanilide yields $C_6H_4 < \begin{smallmatrix} S \\ \parallel \\ N \end{smallmatrix} = \begin{smallmatrix} S \\ \parallel \\ N \end{smallmatrix} CMe$. Although, thus, they failed to obtain dithio-compounds in the last two cases, still they believe that the reactions in every case could be explained only on the assumption that the thioamide group has the structure $RC(NH)SH$.

CHEMICAL ABSTRACTS.

The Catalytic Reduction of Hydrogen Cyanide. SYDNEY BARRATT and ALAN FRANCIS TITLEY (T., 1919, 115, 902—907).

New Method of Preparation of some Polynitro-aromatic Compounds. MARQUEYROL and LORLETTE (*Bull. Soc. chim.*, 1919, [iv], **25**, 370—375).—For the preparation of compounds of the type

of trinitrophenol, the authors recommend that the nitration should be carried out in three stages. The phenol ($\frac{1}{2}$ mol.) is converted into *p*-phenolsulphonic acid, which is then diluted with water and poured into a cold aqueous solution of sodium nitrate, the product being sodium 2-nitrophenol-4-sulphonate. To this solution, nitric acid ($\frac{1}{2}$ mol.) is then added, a mixture of 2:4-dinitrophenol and sodium 2:6-dinitrophenol-4-sulphonate being obtained. After cooling, the dinitrophenol is separated by filtration, and may be further nitrated, and to the filtrate more nitric acid ($\frac{1}{2}$ or 1 mol.) is added, and the liquid brought to the boil. By this means, very pure picric acid is obtained with a good yield. This procedure is of advantage in that practically no nitrous fumes are liberated, and but little more than the theoretical quantities of sulphuric and nitric acids are required.

This method may be applied to commercial cresol. In the first stage, any *o*-cresol present yields *o*-cresol-5-sulphonic acid, the *m*-cresol gives *m*-cresol-6-sulphonic acid, and the *p*-cresol gives *p*-cresol-3-sulphonic acid. In the next stage, from these sulphonic acids are formed, respectively, the 3-nitro-derivative, a mixture of the 2-nitro- and 4-nitro-compounds, and the 5-nitro-derivative. In the third stage, the *o*- and *p*-cresols will yield simply their 3:5-dinitro-derivatives, which are insoluble in water, and may be filtered off, whilst from the *m*-cresol there is obtained sodium 2:4-dinitro-*m*-cresol-6-sulphonate, which is soluble. The latter compound, when boiled with nitric acid, gives trinitro-*m*-cresol.

It is suggested that the nitrosulphonic acids of the three cresols may be separated through their potassium salts, since that from *p*-cresol is only sparingly soluble in water and is formed in the cold; that from *o*-cresol is only sparingly soluble, and is not formed in the cold, but only at 50°; whilst that from *m*-cresol is soluble in water and is only formed at 60°. W. G.

Preparation of 2:4-Dinitrophenol by Direct Nitration of Phenol. MARQUEYROL and LORLETTE (*Bull. Soc. chim.*, 1919, [iv], 25, 375).—If phenol is liquefied by the addition of 30 grams of water to 94 grams of the phenol, and this liquid is slowly added to a mixture of 400 c.c. of sulphuric acid (D 1.58) and 270 c.c. of nitric acid (D 1.33), kept well stirred, and cooled until the whole of the phenol is added, the temperature then being allowed to rise to 100°, a yield of 71% of 2:4-dinitrophenol is obtained. W. G.

Oxidation of Phenols. III. Polymerisation of Methylenequinones to Cyclic Dehydrophenols. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, 52, [B], 1392—1402).—Dehydro-1-methyl- β -naphthol is decomposed when heated in xylene solution into 1-methyl- β -naphthol and naphthamethylenequinone, which could not be obtained in the unimolecular state (A., 1915, i, 419); this substance has now been obtained in the form of sulphur-yellow crystals, m. p. 143° (corr.), and is shown to be formed by the condensation of two molecules of the methylenequinone. It appears

to be dehydro- $\alpha\beta$ -dinaphthol-2-ethane (annexed formula), since it yields a *monophenylhydrazone*, shining platelets, m. p. 233° (corr.), and is reduced by zinc dust and acetic acid to $\alpha\beta$ -dinaphthol-2-ethane, m. p. 253° (corr.) (*diacetyl* derivative, monoclinic plates, m. p. 233—234° [corr.]), which is readily reconverted into dehydrodinaphthoethane by oxidation with potassium ferricyanide in dilute alkaline solution.

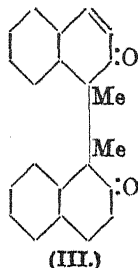
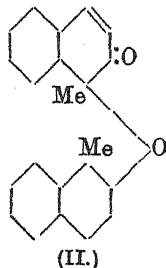
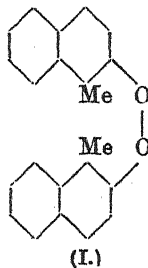
Dehydro-6-bromo-1-methyl- β -naphthol (*loc. cit.*) is similarly decomposed by boiling xylene, yielding bromomethylnaphthol and *dehydrodibromodinaphthoethane*, yellow prisms, m. p. 177° (corr.). The latter gives a *monophenylhydrazone*, small, reddish-brown needles, m. p. 237—238° (corr.), and is reduced to 6:6'-dibromo- $\alpha\beta$ -dinaphthol-2-ethane, needles, m. p. 275° (corr.), which is readily re-oxidised to the parent substance.

Zincke's tetrachloro-*p*-methylenebenzoquinone (A., 1903, i, 757) has been shown to be dehydro-tetrachloro-*p*-cresol (*loc. cit.*) from a study of its power to oxidise quinol; this conclusion is now confirmed by observations of its oxidising action on potassium iodide. Determinations of molecular weight in benzene show an almost complete dissociation of the double molecule either into the radicles, or, more probably, into the methylenequinone and tetrachloro-*p*-cresol.

The authors' investigations lead them to consider that the true methylenequinones with an unsubstituted methylene group are exceedingly active substances which readily polymerise. They are therefore of the opinion that the seven compounds described as such in the literature are either quinol ethers or dehydro-substances, and that a methylenequinone with unsubstituted methylene group has not up to the present been isolated in the unimolecular condition.

H. W.

Oxidation of Phenols. IV. Constitution of the Dehydronaphthols and Preparation of Dehydro- α -bromo- β -naphthol. RUDOLF PUMMERER (*Ber.*, 1919, 52, [B], 1403—1413).—The three following formulæ are possible for dehydro-1-methyl- β -naphthol (compare A., 1915, i, 418):

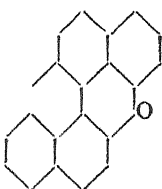
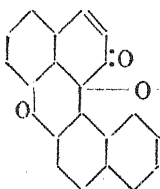


The first explains the ready union of the substance with tri-

phenylmethyl, but is improbable by reason of the yellow colour of the substance and its instability towards permanganate in acetone solution at -40° . The decision between II and III cannot be made with phenylhydrazine, which behaves as a reducing agent. The author has therefore prepared an α -halogen-substituted dehydro- β -naphthol in which, according to II, two halogen atoms must be loosely combined, whilst, according to III, only one is in loose combination. *Dehydro- α -bromo- β -naphthol*, m. p. $115-116^{\circ}$, is prepared by the action of tetrachlorodehydro-*p*-cresol on 1-bromo- β -naphthol; it contains only one reactive bromine atom, since it is hydrolysed in aqueous-alcoholic solution to β -naphthaquinone and 1-bromo- β -naphthol, and is reduced by stannous chloride probably to *α' -bromo- β -hydroxy- $\alpha\beta'$ -dinaphthyl ether*, m. p. $135.5-136.5^{\circ}$ (corr.), in which the α -position adjacent to the hydroxyl group must be occupied, since it does not yield an azo-dye with benzenediazonium chloride. The dibromo-compound must therefore have a constitution analogous to that expressed by formula II.

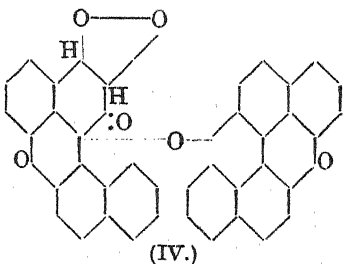
β -Hydroxy- $\alpha\beta'$ -dinaphthyl ether is obtained, amongst other products, by the dehydrogenation of β -naphthol by potassium ferricyanide in alkaline solution (compare following abstract); the first product is probably dehydro- β -naphthol, the keto-form of which is not stable and passes into the corresponding enolic form.

The constitution of dehydro-oxydinaphthalene oxide (Pummerer and Frankfurter, A., 1914, i, 714) is further discussed. It readily decolorises potassium permanganate, and hence cannot be an aromatic peroxide; the diketone-formula is also impossible, for reasons previously given, so that there remains only the annexed formula.

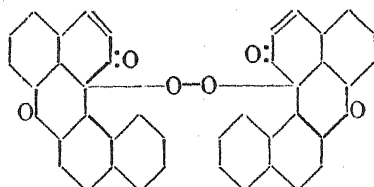


When treated with benzoyl peroxide (subsequent abstract), it absorbs two atoms of oxygen, yielding a compound which is termed a β -peroxide (IV), to distinguish it from the α -peroxide (V) obtained with oxygen. The β -derivative is sharply distinguished from the α -compound by its stability towards

permanganate in pyridine solution and by the lemon-yellow colour



(IV.)



(V.)

common to all *O*-derivatives of hydroxydinaphthalene oxide, whereas the *C*-derivative (α -peroxide) is pale brown. The β -per-

oxide can only be obtained from the solid dehydro-substance; solutions of the latter, even when concentrated, are rapidly decolorised by benzoyl peroxide without separation of the β -peroxide, whilst the α -peroxide is contained among the products, its formation being primarily due to the dissociation of the dehydro-substance into its component radicles (Pummerer and Frankfurter, *loc. cit.*); the possible tautomerism of the latter is again discussed, and the hypothesis advanced previously (*loc. cit.*) satisfactorily explains the more recent phenomena.

H. W.

Oxidation of Phenols. V. Formation of β -Hydroxy- $\alpha\beta'$ -dinaphthyl Ether by the Dehydrogenation of β -Naphthol. RUDOLF PUMMERER and EMIL CHERBULIEZ (*Ber.*, 1919, 52, [B], 1414—1415. Compare preceding abstract).—Oxidation of a solution of β -naphthol in the requisite quantity of aqueous sodium hydroxide solution by means of aqueous potassium ferricyanide leads to a mixture of products from which β -hydroxy- $\alpha\beta'$ -dinaphthyl ether, colourless needles, m. p. 196°, can be isolated in small amount.

H. W.

Oxidation of Phenols. VI. Dehydro-oxydinaphthalene Oxide and Colorimetric Observations of its Dissociation into Radicles. RUDOLF PUMMERER and FRITZ FRANKFURTER (*Ber.*, 1919, 52, [B], 1416—1420. Compare preceding abstracts).—The β -peroxide of dehydro-oxydinaphthalene oxide is prepared by the action of a concentrated solution of benzoyl peroxide in benzene on dehydro-oxydinaphthalene oxide at the ordinary temperature; it forms lemon-yellow, microscopic prisms, m. p. 210° (corr.; decomp.), which are reduced by zinc dust and acetic acid to hydroxydinaphthalene oxide; the latter is also obtained by reduction of the α -peroxide.

The dilutions at which dehydro-oxydinaphthalene oxide is completely dissociated into its radicles have been colorimetrically estimated for a number of solvents (chloroform, benzene, xylene, ethyl ether, ethyl acetate, carbon disulphide, nitrobenzene); the dielectric constant of the solvent appears to have little influence on its dissociating power.

H. W.

Compounds of Arsenic Acid and Catechol. R. F. WEINLAND and JOSEF HEINZLER (*Ber.*, 1919, 52, [B], 1316—1329).—*Catechol semiarsenate*, $\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH})_3\cdot 4\text{H}_2\text{O}$, m. p. about 103° after softening at 60°, is readily obtained in large, colourless crystals when concentrated aqueous solutions of arsenic acid and catechol in molecular proportions varying from 1:½ to 1:3 are mixed. It is slowly hydrolysed in dilute aqueous solutions, more readily in the presence of acids, and is not decomposed by short heating with alkalis. It is stable in diffused light, but darkens on exposure to direct sunlight. It forms beautifully crystalline salts, in which it appears to function as a monobasic acid as far as the experimental evidence at present shows. When titrated with alkali in the

presence of phenolphthalein, the colour change occurs after addition of exactly one equivalent of base, with methyl-orange at a slightly earlier stage; the acid thus appears to be weaker than arsenic acid. The salts are generally prepared by the addition of the base or of a suitable salt of the metal to a concentrated aqueous solution of the acid. The following salts are described: *ammonium salt*, $\left[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3\right]\text{NH}_4$, plates; *potassium salt*, plates or rods; *sodium salt* ($2\text{H}_2\text{O}$), rods, anhydrous, prisms; *silver salt*, minute crystals, very sparingly soluble in water and not sensitive to light; *magnesium salt* ($8\text{H}_2\text{O}$); *calcium salt* ($8\text{H}_2\text{O}$); *barium salt* ($8\text{H}_2\text{O}$); *zinc salt* ($8\text{H}_2\text{O}$); *ferrous salt* ($8\text{H}_2\text{O}$); *nickel salt* ($8\text{H}_2\text{O}$); *cobalt salt* ($8\text{H}_2\text{O}$). With the exception of the barium compound, the salts generally crystallise in cubes. The estimation of water of crystallisation is rendered a little uncertain by the difficulty of drying the substances without decomposition.

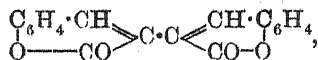
If a considerable excess of catechol is used in the preparation of the ammonium or potassium salts, *compounds* of the formula $3[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]\text{K}(\text{NH}_4)\text{H}_2\cdot\text{C}_6\text{H}_4(\text{OH})_2$ are obtained; catechol is liberated when they are dissolved in hot water, and primary catechol arsenates are formed.

Another *ammonium salt*, which appears to have the composition $3[\text{AsO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O})_3]\text{H}_3\cdot 7\text{NH}_3$, is also described, but the exact analysis is difficult, as it loses ammonia at the ordinary temperature.

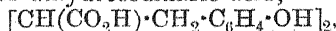
H. W.

The Reduction of *alloCinnamic Acid* and *Coumarin*.

YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1919, No. 444, 97—109).—By reduction of methyl *allocinnamate* with sodium amalgam, phenylpropionic acid (43%), $\beta\gamma$ -diphenyladipic acid, m. p. 175° (6%), and the corresponding *iso-acid*, m. p. 75° (3%), were obtained as their methyl esters. Henle (A., 1906, i, 669), using aluminium amalgam, obtained 55%, 8—9%, and 4—5%, respectively, of the same compounds by reduction of methyl cinnamate. This shows that *allocinnamic* and *cinnamic acids* yield essentially the same reduction products. Sodium amalgam is a better reducing agent than aluminium amalgam, since it reacts more rapidly, and the precipitation of aluminium hydroxide is avoided. Coumarin, as a derivative of *allocinnamic acid*, yields bimolecular reduction products. Dyson (T., 1887, 51, 68) obtained from salicylaldehyde and sodium succinate a dicoumarin,



which he reduced to dihydrocoumaric acid,



and to dihydrocoumarin, m. p. $222\text{—}224^\circ$. Fries and Fickewirth (A., 1908, i, 822) obtained, by reduction of coumarin and dehydration of the resulting tetrahydrodicoumaric acids, two tetrahydrodicoumarins, m. p. 284° and 256° respectively. The former they

designated α , the latter β , and to the acids they assigned the Dyson dihydrocoumaric acid formula shown above. This formulation is incorrect; two coumarin nuclei must necessarily unite in the β -position, whereas Dyson's dihydrocoumarin is linked in the α -position. Its reduction products are derivatives of succinic acid, whilst the products of direct reduction of coumarin are β -disubstituted adipic acids. This was established experimentally by repeating Fries and Fickewirth's preparation of the tetrahydrocoumarins, which were obtained with m. p. 284° and 256° , just as described by those authors, and comparing them with reduction products of dicoumarin prepared as described by Dyson. The latter process yielded two dihydrocoumarins, m. p. 243° and 248° respectively, but when mixed they had m. p. $222-224^\circ$. It was evidently this mixture which Dyson obtained. Neither is identical with either of the tetrahydrocoumarins of Fries and Fickewirth. It is therefore proposed to call Dyson's compound α -dicoumarin, and the two derivatives (of which he had the mixture) α - and β -tetrahydro- α -dicoumarin. The tetrahydro-derivatives of Fries and Fickewirth are, then, to be considered as derivatives of an unknown β -dicoumarin.

CHEMICAL ABSTRACTS.

The Acylsemicarbazides and the Acylhydroxamides (Rectification). J. BOUGAULT (*Bull. Soc. chim.*, 1919, [iv], 25, 384—386).—As a result of further analyses, the author now finds that the compounds obtained by the action of iodine and sodium carbonate on the semicarbazones and oximes of α -ketonic acids, and previously described as acylsemicarbazides and acylhydroxamides (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), do not possess the constitution then assigned to them. Instead of a molecular composition, $R \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$, as given to the acylsemicarbazides, the elements of a molecule of water should be deducted, giving an empirical formula $R \cdot C_2H_2ON_3$, the constitution of which has not been elucidated. Similarly, where the acylhydroxamides were assigned the constitution $R \cdot CO \cdot NH \cdot OH$, the formula should now be written $R \cdot CON$, and their constitution is considered to be either $\begin{array}{c} \text{CPh} \cdot \text{CPh} \\ \parallel \quad \parallel \\ \text{NO} \cdot \text{ON} \end{array}$ or $\begin{array}{c} \text{CPh} \cdot \text{CPh} \\ \parallel \quad \parallel \\ \text{N} \cdot \text{O} \cdot \text{N} \end{array} > \text{O}$. It has been shown that the so-called acylhydroxamide obtained from phenylglyoxylic acid is identical with diphenylglyoxime peroxide. W. G.

Truxillic Acids and Truxones. R. STOERMER and G. FOERSTER (*Ber.*, 1919, 52, [B], 1255—1272).—The recent publication of Stobbe (this vol., i, 329) has induced the authors to describe a series of experiments which are still partly unfinished.

*alloy*Cinnamic acid is transformed by the light of a quartz lamp into β -isotruxillic acid; in sunlight, the same acid is also formed, occasionally accompanied by α -truxillic acid. Depolymerisation of β -isotruxillic and α -truxillic acids occurs when solutions of their sodium salts are exposed to the light of a quartz lamp, *trans*- and *allo*-cinnamic acids being formed from the former acid, cinnamic

and, possibly, *allocinnamic* and γ -truxillic acids from the latter acid. Attempts to polymerise crotonic, fumaric, β -phenylcinnamic, and *cis*- or *trans*-*p*-methoxycinnamic acids by sunlight were unsuccessful; β -methylcinnamic acid, however, gave dimethyltruxillic acid, m. p. 217—218°.

α -Truxone, m. p. 293°, is conveniently prepared by the action of aluminium chloride on a solution of α -truxillyl chloride in carbon disulphide; the dioxime, m. p. above 300°, is converted by methyl sulphate into the *dimethyl ether*, m. p. 214°. The molecular weight of the latter has been determined in benzene solution, and the results confirm the formula, $(C_9H_6O)_2$, for truxone. γ -Truxillic acid could not be converted into a truxone by sulphuric acid, but yielded α -truxone with aluminium chloride; β - and δ -isotruxillic acids were either unchanged or merely sulphonated by sulphuric acid.

α - and γ -*Diphenyltruxones* are prepared by the action of fuming sulphuric acid on β -phenylcinnamic acid or β -hydroxy- β -phenylhydrocinnamic acid, and are separated by fractional crystallisation from acetone or from a mixture of alcohol and acetic acid; the former crystallises in rods or plates, m. p. 253°, whilst the latter has m. p. 224°, and is converted when heated at about 225° into the α -derivative. The following derivatives are described: *α -diphenyltruxone monoxime*, six-sided crystals, m. p. 273·5° (*methyl ether*, colourless needles, m. p. 208°); *α -diphenyltruxone dioxime*, needles, m. p. 262°; *γ -diphenyltruxone monoxime*, needles, m. p. 235° (*methyl ether*, m. p. 170°); *γ -diphenyltruxone dioxime*, m. p. 270·5—271°. The hydroxylamino-group is readily removed by treatment of the oximes with alcohol at 100°, the corresponding truxones being regenerated. *α -Diphenyltruxone monophenylhydrazone* forms yellow crystals, m. p. 153—154°, whilst the monophenylhydrazone of the γ -compound has m. p. 128—129°. Attempts to reduce the truxones completely by Clemmensen's method, by sodium amalgam, zinc and acetic acid, or zinc and potassium hydroxide were unsuccessful, the process coming to an end with the production of the diol. In these circumstances, γ -diphenyltruxone yields *α -diphenyltruxandiol*; isomerisation is not induced by hydrochloric acid or potassium hydroxide alone, so that the nascent hydrogen appears to have an isomerising as well as a reducing action. *α -Diphenyltruxandiol* has m. p. 234·5°; the *monoacetate* (possibly not quite pure) melts at 235—237°, the *diacetate* at 215—216°. The α - and γ -*diphenyltruxanes* were, however, prepared from the corresponding truxones by the action of hydrazine and sodium ethoxide; the former has m. p. 201—202°. *γ -Diphenyltruxone dihydrazone* forms small crystals, m. p. 254°, and is converted by sodium ethoxide into a mixture of α -diphenyltruxane and γ -diphenyltruxane, m. p. about 169—171°, but the latter could not be prepared in the pure condition on account of lack of material. The latter is completely converted into the α -isomeride when heated for five hours at a temperature slightly above its melting point.

H. W.

Constitution of Bile Acids. II. Dehydrocholanic Acid.

W. BORSCHKE (*Ber.*, 1919, **52**, [B], 1353—1365. Compare Borsche and Rosenkranz, this vol., i, 276).—Further experiments with dehydrocholanic acid lead the author to adopt Schenk's view of its constitution, and thus to consider it as a triketocarboxylic acid containing the $\cdot\text{CO}\cdot\text{CH}_3$ group; all attempts to identify the presence of an aldehydic group were unsuccessful, whilst it has been found possible to condense the substance with aromatic aldehydes, thus obtaining conclusive evidence of the presence of the $\cdot\text{CO}\cdot\text{CH}_3$ group. One of the carbonyl groups of dehydrocholanic acid is more reactive than the remaining two, and thus gives rise to acetals when the acid is esterified, whilst also it is the first to suffer reduction; the compound thus formed, which was previously described as deoxydehydrocholanic acid, is now designated β -dehydrodeoxycholanic acid, to avoid confusion with the primary product of the oxidation of deoxycholanic acid.

Methyl dehydrocholanate, $\text{C}_{25}\text{H}_{36}\text{O}_5$, is prepared by the esterification of dehydrocholanic acid in the presence of a considerable amount of hydrogen chloride or sulphuric acid; it crystallises in silky needles, m. p. 241—242°, which are very sparingly soluble in methyl alcohol. It forms a *trioxime*, leaflets, m. p. 265—266°, and a *triacetyl* derivative, which gradually melts from about 60°. *Methyl dehydrocholanate dimethylacetal*, $\text{C}_{27}\text{H}_{42}\text{O}_6$, is formed by treating the ester or the acid with methyl alcohol containing 1% of hydrogen chloride or 3% of sulphuric acid; it forms long needles, m. p. 140°, and is freely soluble in warm methyl alcohol. It is reconverted into the ester by concentrated methyl-alcoholic solutions of mineral acids, and is hydrolysed to dehydrocholanic acid by alkali. With hydroxylamine, it gives the trioxime of methyl dehydrocholanate. The acetal nature of the substance is proved by the fact that methyl alcohol is readily eliminated when it is heated, and that it yields an *enol ether*, $\text{C}_{26}\text{H}_{34}\text{O}_5$, colourless leaflets, m. p. 173—174°, b. p. 333—334°/16 mm. Methyl-alcoholic potassium hydroxide solution converts it into dehydrocholanic acid, whilst hydroxylamine transforms it into the trioxime of methyl dehydrocholanate. It readily absorbs bromine, but methyl bromide appears to be eliminated simultaneously. A similar substance, m. p. 170—172° (decomp.), appears to be formed by the action of a 2% solution of sulphuric acid in ethyl alcohol on dehydrocholanic acid, but the product is readily converted into ethyl dehydrocholanate, m. p. 221°.

β -Deoxydehydrocholanic acid, needles, m. p. 176°, is prepared mixed with unchanged acid, and cholanecarboxylic acid by the reduction of dehydrocholanic acid by amalgamated zinc and hydrochloric acid; it crystallises also with $1\text{H}_2\text{O}$, m. p. 115°. The *ethyl* ester crystallises in colourless needles, m. p. 152—153°, and yields a *dioxime*, pearly leaflets, m. p. 242° (decomp.).

Cholanecarboxylic acid, m. p. 160°, is obtained in 55—60% yield by the reduction of dehydrocholanic acid by Clemmensen's method. The following derivatives have been prepared: *ethyl* ester, colour-

less, coarse needles, m. p. 92°; *chloride*, m. p. 128°; *amide*, minute, hexagonal prisms, m. p. 75°. H. W.

Preparation and Uses of Semi-oxamazide. L. G. RADCLIFFE (*Perfumery and Essen. Oil Rec.*, 1919, 10, 39—42).—During a study on certain aromatic aldehydes, it became necessary to prepare their semi-oxamazones, and preliminary thereto the requisite semi-oxamazide. Detailed descriptions are accordingly given for the preparation of ethyl oxalate, oxamethane, and the finished reagent. Many of the semi-oxamazones described had been previously prepared by Kerp and Unger (A., 1897, i, 269), and include those of benzaldehyde, *p*-toluic, *p*-isopropylbenzoic, anisic, cinnamic, salicylic and phenylacetic aldehydes, vanillin, piperonal, citral and furfuraldehyde, acetophenone, phenyl ethyl ketone, styryl methyl ketone, benzophenone, and menthone. CHEMICAL ABSTRACTS.

A New Method of Obtaining Bicyclic Ketones. FÉLIX TABOURY and MARCEL GODCHOT (*Compt. rend.*, 1919, 169, 62—64).—*cyclopentanone* and *cyclohexanone* and their homologues are readily converted into unsaturated bicyclic ketones when their vapours are passed over calcium hydride. Calcium carbide is not so satisfactory a condensing agent, only giving a good result with *cyclopentanone* out of the four ketones examined. W. G.

Synthesis of Ketimines by Catalytic Methods. GEORGES MIGNONAC (*Compt. rend.*, 1919, 169, 237—239).—It has been found possible to prepare certain ketimines by passing the vapour of the ketone, along with ammonia, over thorium oxide at 300—400°, the temperature varying with the ketone used. This method is not applicable to purely aliphatic ketones, owing to the readiness with which their ketimines undergo condensation. Successful results were obtained with acetophenone, propiophenone, and benzophenone, but only a very small yield was obtained from *cyclohexanone*. W. G.

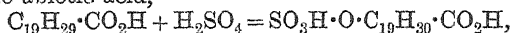
Hydrogenation of Piperonal Ketone and of Dipiperonal Ketone. VAVON and FAILLEBIN (*Compt. rend.*, 1919, 169, 65—67).—The method with platinum black previously described (compare A., 1914, i, 694) may be used satisfactorily for the hydrogenation of piperonal and dipiperonal ketones. In the latter case, the reaction takes place in two stages, giving first *dihydropiperonal ketone*, $\text{CH}_2\langle\text{O}\rangle\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\langle\text{O}\rangle\text{CH}_2$, m. p. 99°, and then the fully saturated *ketone*, $\text{CO}(\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\langle\text{O}\rangle\text{CH}_2)_2$, m. p. 55°. Both the yellow and the white forms of piperonal ketone, as described by Haber (compare A., 1891, 704), on hydrogenation give the same saturated *ketone*, m. p. 51°, b. p. 168°/13 mm., giving an *oxime*, m. p. 98°, and a *semicarbazone*, m. p. 166°. The authors consider that the yellow form, m. p. 107°,

as described by Haber, is but an impure specimen of the white form, m. p. 111°. W. G.

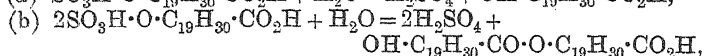
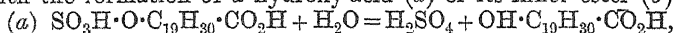
Alcoholysis of Balsams. ERNEST FOURNEAU and MARIO CRESPO (*Bull. Soc. chim.*, 1919, [iv], 25, 386—389).—The process, which consists in boiling the balsam for six hours with an equal weight of ethyl alcohol containing 3% of hydrogen chloride, neutralising the product with sodium carbonate, and distilling off the esters and alcohols in steam, does not attack the resins. The esters and alcohols are separated by fractional distillation. The results indicate that the balsams are a mixture of cinnamyl and benzyl cinnamates and benzoates in varying proportions, and resins.

W. G.

The Action of Sulphuric Acid on Colophony. AD. GRÜN (*Chem. Umschau Fett. Ind.*, 1919, 26, 77—79).—When colophony is mixed with light petroleum and treated with sulphuric acid for several hours at -5° , the sulphuric acid combines with the double bond of the abietic acid,



and on boiling the sulphuric acid ester with water, it is decomposed with the formation of a hydroxy-acid (a) or its inner ester (b):



or a mixture of the two products. From the acid value and acetyl value of the product obtained in one experiment, it was calculated that it consisted of 64.1% of the inner ester, 26.5% of unaltered abietic acid, and 9.4% of unsaponifiable matter. Esterification of colophony with sulphuric acid in the presence of methyl alcohol, and decomposition of the product by boiling with water, yields only the methyl ester of abietic acid, with not more than a trace of hydroxy-acid. The methyl ester absorbs only two molecules of halogen when treated with Wijs' iodine chloride solution, whereas the free abietic acid absorbs three molecules. [See also *J. Soc. Chem. Ind.*, 1919, 589A.] C. A. M.

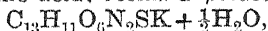
Researches on Chlorophyll. XXV. Phytol. II. RICHARD WILLSTÄTTER, OTTO SCHUPPLI, and ERWIN W. MAYER (*Annalen*, 1919, 418, 121—147).—The supposed difference between the oxidation products of crude and distilled phytol (compare Willstätter, Mayer, and Hüni, A., 1911, i, 144) is found to be non-existent, α - and β -phytols containing the double linking in the same position. After distillation, phytol does, however, lose water the more readily, especially when heated with phthalic anhydride or acetic acid, probably owing to the existence of two geometrically isomeric forms of the alcohol. The purest preparations of the ketone, obtained by oxidising phytol, have compositions agreeing well with the formula $\text{C}_{15}\text{H}_{30}\text{O}$, but they all contain oxygen-rich admixtures, which are most persistently retained. Repeated conversion of the ketone into its 1-naphthylhydrazine-4-sulphonic acid derivative, followed by

crystallisation and hydrolysis, yields a purified product, the formula of which is most probably $C_{17}H_{34}O$. The action of ozone or chromic acid on this product gives, not a lower ketone, but simply admixtures of increasing oxygen content. The fatty acid occurring with the ketone, and also formed from the latter on oxidation, has not the formula formerly assumed, namely, $C_{14}H_{28}O_2$, but is most probably $C_{16}H_{32}O_2$. Phytol therefore contains the double linking between the third and fourth carbon atoms, and phytenic acid, which is readily converted into an isomeric lactone, should possess the formula $C_{15}H_{31} \cdot CMe \cdot CMe \cdot CO_2H$, since Fichter, Kiefer, and Bernouilli's results (A., 1910, i, 88) show that alkyl groups in the α - and β -positions produce instability of the Δ^1 -acids towards 60% sulphuric acid, being transformed thereby completely into lactones.

The hypothetical structure suggested for phytol by Willstätter, Mayer, and Hüni (*loc. cit.*) thus becomes improbable, the occurrence of derivatives with branched carbon atom chains and of none with normal chains among the oxidation products indicating complex branching of the carbon atom skeleton of phytol.

The purification or isolation of ketones or aldehydes by converting them into derivatives which contain an acidic group, and hence yield salts capable of crystallisation, is illustrated by various examples.

Thus, *methyl-ethyl-ketone-phenylhydrazone-m-carboxylic acid*, $C_{11}H_{14}O_2N_2$, obtained by the action of *m*-hydrazinobenzoic acid on the ketone, crystallises in plates, m. p. 143° . *Methyl-hexyl-ketone-phenylhydrazone-m-carboxylic acid* does not crystallise, but its *ammonium salt*, $C_{15}H_{25}O_2N_3$, crystallises in bundles of leaflets, m. p. 151° . *Methyl-nonyl-ketone-phenylhydrazone-m-carboxylic acid* forms spherical, crystalline aggregates, m. p. 93° , but is unstable; its *ammonium salt*, $C_{18}H_{31}O_2N_3$, crystallises in colourless leaflets, m. p. 146 — 147° (frothing). *Methyl-stearyl-ketone-phenylhydrazone-m-carboxylic acid*, $C_{26}H_{44}O_2N_2$, forms spherical, crystalline nodules, m. p. 83 — 84° (decomp.), and its *ammonium salt*, which crystallises in leaflets, m. p. 136° (decomp.), is, like the compounds described above, converted quantitatively into the ketone by boiling 17% sulphuric acid. *Carvone-phenylhydrazone-m-carboxylic acid*, $C_{17}H_{20}O_2N_2$, separated from commercial carvone mixed with four times its quantity of limonene, forms rhombic plates, m. p. 158° . *Methyl-nonyl-ketone-1-naphthylhydrazone-4-sulphonic acid* gives a crystalline *sodium salt*, m. p. 250 — 252° (decomp.). *Methyl-succinic-acid-1-naphthylhydrazone-4-sulphonic acid*, obtained by hydrolysing the ketone-1-naphthylhydrazone-4-sulphonic acids by means of methylsuccinic acid, forms a *potassium salt*,



which crystallises in yellow leaflets, loses its water of crystallisation at 100 — 110° , and has m. p. 203 — 204° (decomp.).

When treated with potassium 1-naphthylhydrazine-4-sulphonate, the ketone obtained by oxidising phytol by means of either ozone or chromic acid gives a *potassium salt*, $C_{27}H_{41}O_3N_3SK$, which crystallises in slender, white needles sintering at 140° , m. p.

164—165° (decomp.). The ketone yields a semicarbazone, $C_{18}H_{37}ON_3$, m. p. 66·5—67°. The pure ketone, $C_{17}H_{34}O$, obtained by hydrolysis of either the above potassium salt or the semicarbazone, contains 3—4% of the enolic modification, and forms a colourless, mobile liquid, b. p. 175—175·5°/11 mm., D_4^{20} 0·844, D_4^{20} 0·834, n_D^{20} 1·44516. Its *oxime*, $C_{17}H_{35}ON$, is a colourless, viscous oil, b. p. 201·6—202°/9 mm., D_4^{20} 0·879. The alcohol, $C_{17}H_{36}O$, obtained by reducing the ketone by means of sodium and alcohol, forms a viscous oil, b. p. 176—177·5°/10 mm., D_4^{20} 0·847, D_4^{20} 0·837, n_D^{20} 1·45037. When heated with phosphoric oxide, this alcohol gives the olefine, $C_{17}H_{34}$, b. p. 288—291°/719 mm., 153—155·5°/10 mm., D_4^{20} 0·790, which in acetic acid solution is converted by platinum and hydrogen into the corresponding paraffin, $C_{17}H_{36}$, b. p. 161—162°/15 mm., D_4^{20} 0·794, D_4^{20} 0·780, n_D^{20} 1·43763. This paraffin is not identical with the saturated hydrocarbon previously described as a product of the fractional distillation of the crude ketone. The formation of the hydrocarbon, $C_{15}H_{32}$, b. p. 131—132°/13 mm., 249—250°/718 mm., as a by-product of the hydrolysis of phytol ozonide is confirmed.

The action of ozone on the ketone in ethyl chloride solution yields the peroxide, $C_{17}H_{34}O_2$, as an oil, D_4^{20} 0·899, D_4^{20} 0·885, with a piercing odour. A considerable part of the oxygen taken up is lost when the peroxide is distilled, even under diminished pressure. It gives an intense reddish-brown coloration with titanium sulphate and liberates iodine, but not in the calculated proportion, from acid or neutral potassium iodide solution. Even the most active reducing agents convert the peroxide, not into the original ketone, but into products containing more oxygen than this; from these products or from the peroxide itself, the pure ketone may, however, be obtained by way of the semicarbazide. Similar behaviour is exhibited by *methyl nonyl ketone peroxide*, $C_{11}H_{22}O_2$, which forms a colourless oil of piercing odour.

The oily, fatty acids formed together with formic acid by oxidising phytol in various ways, by oxidising the ketone, $C_{17}H_{34}O$, by means of either chromic acid or alkaline bromine solution, or by boiling the ozonide of the hydrocarbon, $C_{17}H_{34}$, apparently range in formula from $C_{16}H_{32}O_2$ to $C_6H_{12}O_8$. The ozonide yields also a *hydrocarbon*, $C_{11}H_{20}$ (?), b. p. 114—117°/11 mm., 241—244°/723 mm., and this, when oxidised, gives a mixture of carboxylic acids and a carbonyl compound, (? ketone), $C_{12}H_{24}O$, which is a mobile liquid, b. p. 84°/14 mm., 188—189°/726 mm., with the odour of lemons, and forms a *semicarbazone*, m. p. 121—123°.

Fractionation of the acids formed on degradation of the olefine, $C_{17}H_{34}$, and purification by means of the *silver* salt, m. p. 191—193°, gives mainly the acid, $C_{16}H_{32}O_2$, b. p. 201—204°/13 mm., D_4^{20} 0·901, D_4^{20} 0·887, n_D^{20} 1·44967; the corresponding *amide*, $C_{16}H_{33}ON$, forms leaflets, m. p. 46·5—48·5°.

T. H. P.

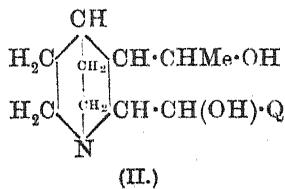
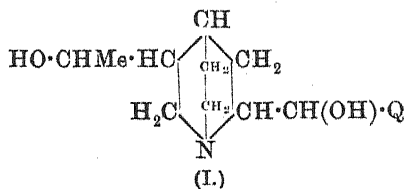
β -Homochelidonine. KANJIRO MOMOYA (*J. Pharm. Soc. Japan*, 1919, No. 444, 110—118 and 6—8).—Protopine and β -homo-

chelidonine, occurring in the alcoholic extract of the roots of *Macleya cordata*, are best separated by means of dilute aqueous ammonia. At 13°, the solubility of protopine in 1% aqueous ammonia is 1.15 grams per litre, whilst that of β -homochelidonine is 6.0 grams per litre. Still further purification is possible through the hydrochlorides; 100 c.c. of water at the ordinary temperature dissolve 14.5 grams of β -homochelidonine hydrochloride, but only 0.7 gram of protopine hydrochloride.

β -Homochelidonine yields two crystalline compounds with methyl iodide, one ($1\text{H}_2\text{O}$), easily soluble, m. p. 198°, the other ($3\text{H}_2\text{O}$), sparingly soluble, m. p. 211°. With methyl sulphate, it yields a *methosulphate* ($3\text{H}_2\text{O}$), m. p. 215°. With mercuric acetate, it yields a new base, *dehydro- β -homochelidonine*, which melts at 136°, re-solidifies, and melts again at 203—204°. It is optically inactive, dissolves in ethyl alcohol and in chloroform, but is sparingly soluble in water. By oxidation with potassium permanganate, it yields *m*-hemipinic acid and an acid, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{N}$, which was not further studied.

CHEMICAL ABSTRACTS.

Cinchonidine. E. LÉGER (*Compt. rend.*, 1919, 169, 67—70).—With hydrobromic acid (D 1.5), cinchonidine yields *hydrobromocinchonidine hydrobromide*, m. p. 95°. When heated for forty-eight hours with 50% sulphuric acid, cinchonidine gives *hydroxydihydrocinchonidine*, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2$, m. p. 242—243° (corr.), $[\alpha]_D - 101.7^\circ$ (in alcohol), giving a *diacetyl* derivative. It is formed by the addition of the elements of water to the grouping $\text{CH}_2\text{:CH}$ to give the grouping $\text{CH}_2\text{CH(OH)}$. When heated with 70% sulphuric acid at 115° for ten hours, hydroxydihydrocinchonidine yields *apocinchonidine* and β -cinchonidine, thus differing from the oxydihydrocinchonines, which give cinchonigine, cinchoniline, and *apocinchonine*. Based on these observations, the author suggests for hydroxydihydrocinchonidine and α - and β -hydroxydihydrocinchonines the constitutions indicated in formulæ I and II respectively, where Q represents the quinoline residue:

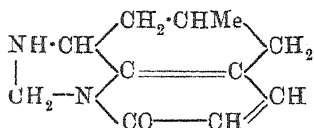


W. G.

Constitution of Cytisine. ERNST SPÄTH (*Monatsh.*, 1919, 40, 15—33).—The author discusses previous publications on the constitution of cytisine (Partheil, A., 1893, i, 119; 1894, i, 558; 1895, i, 119, 254; Freund and Friedmann, A., 1901, i, 288; Freund, A., 1904, i, 263; Freund and Horkheimer, A., 1906, i, 302), more particularly those of Ewins (T., 1913, 103, 97) and Freund and Gauff

(*Arch. Pharm.*, 1918, **256**, 33). The author shows (following abstract) that the cytosoline obtained by Freund by the action of hydriodic acid and red phosphorus on cytosine is 2-hydroxy-6:8-dimethylquinoline. As regards the presence or absence of the quinoline ring in the cytosine molecule, the assumption that the pyridine or benzene nucleus of cytosoline arises by extension of a five-membered ring is an improbable one; further, van de Moer's reaction (A., 1891, 946; also Gorter, A., 1896, ii, 344) indicates distinctly the presence of an α -pyridone residue in cytosine. The 6- and 8-methyl groups of cytosoline may exist in the same positions in cytosine, or, as Ewins suggested (*loc. cit.*), that in the 6-position may have arrived by migration during the conversion of cytosine into cytosoline. The oxygen atom most probably occupies corresponding places in the two molecules. In cytosine, the oxygen atom exists in the form of neither hydroxyl, nor normal keto-group, nor as a bridge; the assumption that it occupies the same position as in cytosoline renders probable its occurrence as an acetylaminocarbonyl group, as in α -pyridone. Since cytosine exhibits marked resistance towards reducing agents, the assumption is justified that the two double linkings form a conjugated pair in a single ring.

On the basis of the above considerations, the fourteen possible structures for the cytosine molecule are discussed, the decision in favour of the annexed formula resting on the apparent formation



of isovaleric acid by the action of barium permanganate on cytosine; this action is to be investigated further when a larger supply of cytosine is available. The similarity of this structure to that of leucine, which frequently occurs free in the

Papilionaceae, suggests that this amino-acid may be the parent substance of the cytisine.

Van de Moer's reaction is given by a number of derivatives of 2-pyridone, especially with 1-methyl-2-pyridone, and also, though less intensely, with 1-methyl-2-quinolones and 1-methyl-2-hydroxyquinolines. The reaction is also shown by 2-hydroxyquinoline, 2-hydroxy-6-methylquinoline, 2-hydroxy-8-methylquinoline, 2-hydroxy-6 : 8-dimethylquinoline, 2-keto-1 : 6-dimethyl-1 : 2-dihydroquinoline, 2-keto-1 : 8-dimethyl-1 : 2-dihydroquinoline, and 2-keto-1 : 6 : 8-trimethyl-1 : 2-dihydroquinoline. Negative results are obtained with hydrocarbostyryl, its 1-methyl derivative, and 4-hydroxyquinoline.

1-Methylhydrocarbostyryl, C_9H_9ONMe , prepared from carbostyryl, sodium methoxide, and methyl sulphate, forms an oil, b. p. 165–166°/13 mm., and is difficult to demethylate by means of hydriodic acid.

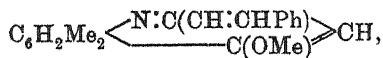
Zerewitinov's method of estimating active hydrogen gives with cytosine an amount of methane corresponding with one atom of active hydrogen, a similar result being obtained with cytosoline.

T. H. P.

Synthesis of Cytisoline. ERNST SPÄTH (*Monatsh.*, 1919, 40, 93—128).—Cytisoline (Freund, A., 1904, i, 263) is proved to be 2-hydroxy-6:8-dimethylquinoline (compare Ewins, T., 1913, 103, 97) by the following method. The additive compound obtained by warming 6:8-dimethylquinoline with methyl sulphate is oxidised by potassium ferricyanide and aqueous sodium hydroxide solution to 2-keto-1:6:8-trimethyl-1:2-dihydroquinoline, $C_{12}H_{13}ON$, faintly yellow crystals, m. p. 71—72°, which is converted by phosphorus pentachloride and a little phosphoryl chloride at 135—140° into methyl chloride and 2-chloro-6:8-dimethylquinoline, long needles, m. p. 56°. The heating should not be prolonged after methyl chloride ceases to be evolved; if it is continued for six hours, the product is a dichlorodimethylquinoline, long needles, m. p. 108—109°. 2-Chloro-6:8-dimethylquinoline is converted into 2-hydroxy-6:8-dimethylquinoline by heating with water at 240° for two hours, or, better, with methyl-alcoholic sodium methoxide at 100° for forty-five minutes, the resulting 2-methoxy-6:8-dimethylquinoline being easily converted into 2-hydroxy-6:8-dimethylquinoline by heating with concentrated hydrochloric acid at 210—220° for two hours, or simply by evaporation with hydrochloric acid and subsequent heating on the water-bath.

The identity of 2-hydroxy-6:8-dimethylquinoline, m. p. 201—202°, with cytisoline (m. p. 199°, according to Freund, *loc. cit.*) is shown by the m. p. of the mixture, 200—201°, by the conversion of each into identical chloro-, methoxy-, nitro-, and tetrahydro-derivatives, and by the formation of cytisinic acid from each by oxidation with chromic and acetic acids.

Other substances were examined in the course of the investigation. 4-Hydroxy-6:8-dimethylquinoline, needles, m. p. 221°, softening at 219°, was obtained as follows. 4-Hydroxy-2:6:8-trimethylquinoline, m. p. 263—264°, prepared from *m*-4-xylydine and ethyl acetoacetate by Conrad and Limpach's method, was converted in warm methyl-alcoholic solution by methyl sulphate and sodium hydroxide into 4-methoxy-2:6:8-trimethylquinoline, pearly leaflets, m. p. 111—112°, which is much more difficultly hydrolysed by hydrochloric acid than are the 2-methoxyquinolines. It reacted with benzaldehyde at 135—140° in the presence of zinc chloride to form 4-methoxy-2-styryl-6:8-dimethylquinoline,



trichroic needles, m. p. 137—138°, which in glacial acetic acid solution containing a little concentrated sulphuric acid was oxidised by potassium permanganate solution, yielding a quinolinecarboxylic acid. This was not isolated in the pure state, but was converted by evaporation with concentrated hydrochloric acid into 4-hydroxy-6:8-dimethylquinoline-2-carboxylic acid, m. p. 250° (decomp.), from which 4-hydroxy-6:8-dimethylquinoline was obtained by heating in a vacuum at 260—280°. The last compound yielded 6:8-dimethylquinoline by distillation with zinc dust, and thus the proof

was furnished that the methyl group in position 2 in 4-methoxy-2:6:8-trimethylquinoline entered into reaction with benzaldehyde.

2-Hydroxy-6-methylquinoline, needles, m. p. 232—233°, and *2-hydroxy-8-methylquinoline*, needles, m. p. 219—220°, were prepared from 6-methylquinoline and 8-methylquinoline respectively in the same way as 2-hydroxy-6:8-dimethylquinoline above; the intermediate compounds are, in the first case, *2-keto-1:6-dimethyl-1:2-dihydroquinoline*, crystals, m. p. 84—85°, *2-chloro-6-methylquinoline*, needles, m. p. 114—115°, and *2-methoxy-6-methylquinoline*, m. p. 63°, and, in the second case, *2-keto-1:8-dimethyl-1:2-dihydroquinoline*, m. p. 92—93°, b. p. 198—198.5°/13 mm., *2-chloro-8-methylquinoline*, needles, m. p. 60—61°, and *2-methoxy-8-methylquinoline*, b. p. 142—143°/18 mm. C. S.

Harmine and Harmaline. III. and IV. WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON (T., 1919, 115, 933—967; 967—972).

An Anomaly in the Solubility of Sparteine. A. VALEUR (*Bull. sci. pharmacol.*, 1919, 26, 145—151).—Mixing aqueous solutions of sodium carbonate and sparteine sulphate results in a slight turbidity, separation of supernatant oily layer, or complete transparency, depending on concentration and temperature. Increase in temperature causes decreased solubility, attributed to the abnormal solubility of basic sparteine sulphate, produced by the action of sodium carbonate on the neutral sulphate. Sparteine alone shows abnormality; 0.496% solution becomes turbid at 12.5°, 0.18% solution at 50°. Solutions of 0.13% or lower do not develop turbidity at the b. p. The solubility is decreased by sodium carbonate, thus in 5% solution, a 0.03% solution of sparteine becomes turbid on boiling. Using progressively regularly increasing amounts of pure sparteine ($[\alpha]_D^{20} 46'$) in 5% sodium carbonate, the author found that the temperature at which the solutions began to become turbid was regularly decreased by 2.5° with each increase in 0.01% of sparteine in concentrations between 0.09% and 0.18%, the temperatures ranging between 47.5° and 25°. Above or below these temperatures, irregularities appeared. A curve is presented. Variations in the strength of the carbonate solution caused appropriate variations in the general level of the curves, although they were found to run parallel to that obtained with the 5% sodium carbonate solution. The method consisted in placing the sample in a test-tube with thermometer in a water-bath and observing the exact temperature of the appearing turbidity. It was necessary to work with carefully filtered solutions, to use either a new tube for each test, or to wash the tube with acid, water, and the new solution to be tested. Wide discrepancies of earlier results as to the solubility are due to lack of appreciation of the effect of temperature changes. The author prepared a solution of sparteine sulphate by adding an excess to water at 10.8°, keeping for two days, centrifuging, and filtering, and he determined the solubility by titration

with 0.1*N*-hydrochloric acid, using methyl-orange, by precipitation with silicotungstic acid, by precipitation with picric acid, and by observing the temperature of appearing turbidity in 5% sodium carbonate. The results coincide, and give about 0.32% as the solubility of the compound at 22°.

CHEMICAL ABSTRACTS.

Constitution of the Dialkyltetrahydrodipyridyls. BRUNO EMMERT (*Ber.*, 1919, 52, [B], 1351—1353).—It was observed by Hofmann (*A.*, 1881, 921) that unstable, dialkyltetrahydrodipyridyls are formed by the action of sodium amalgam on alkylpyridinium haloids, and it was assumed that the pyridine nuclei were united in the α -position. The author has obtained similar substances by the electrolysis of alkylpyridinium salts and by the action of water on sodium pyridine (*A.*, 1909, i, 602; 1917, i, 221), and has therefore endeavoured to deduce their composition with greater certainty. Attempts to reduce *NN'*-dibenzyltetrahydrodipyridyl to the corresponding dipiperidyl were unsuccessful by reason of the tendency of the substance to resinify, but, on distillation with zinc dust, toluene and 4:4'-dipyridyl were obtained. The presence of 2:2'-dipyridyl could not be detected, so that, contrary to Hofmann's assumption, the pyridine nuclei in such compounds are united in the 4-position.

H. W.

Isomerism among Derivatives of Indazole. K. VON AUWERS (*Ber.*, 1919, 52, [B], 1330—1339).—The recent communications of Harries (this vol., i, 131) and Freund and Kessler (this vol., i, 283) on isomerisation among heterocyclic bases have induced the author to publish a preliminary account of investigations of a similar nature which are being carried out in his laboratory.

1-Acetylintdazole, $C_6H_4 \begin{smallmatrix} \text{CH} \\ \text{N} \end{smallmatrix} \text{NAc}$, is prepared by the Beckmann transformation of *o*-aminobenzaldoxime, but the yields in different experiments vary greatly; it has m. p. 169—171°, b. p. 191°/15 mm. (slight decomp.). The sparingly soluble *nitrate* crystallises in small, shining needles grouped in rosettes, whilst the *compound* with mercuric chloride forms flat, shining needles. 1-Acetylintdazole is readily converted by alkali hydroxide or by boiling water into the *N*-acetyl derivative of *o*-aminobenzaldoxime or into the oxime itself. 2-Acetylintdazole, $C_6H_4 \begin{smallmatrix} \text{OH} \\ \text{N} \end{smallmatrix} \text{NAc}$, exists in two forms.

The stable modification, long, transparent, oblique prisms, m. p. 42—43°, b. p. 260°, is formed by the action of acetic anhydride on indazole, and is rapidly hydrolysed by warm acids or alkali hydroxides; it yields a double *compound* with mercuric chloride. The labile *modification* crystallises in needles or plates, m. p. 106°, and is prepared by the action of acetyl chloride on an ethereal suspension of the silver salt of indazole or by acetylation of indazole with acetyl chloride in the presence of pyridine. It is converted into the stable derivative, m. p. 42°, when distilled under diminished

pressure, by crystallisation from solvents of moderately high boiling point, and, slowly, at the ordinary temperature.

The *N*-alkylindazoles have been investigated by Fischer and Tafel (A., 1885, 541), who prepared the 2-alkyl derivative by heating indazole with alkyl iodides. When, however, indazole is heated with alkyl iodides and sodium in the presence of methyl or ethyl alcohol, mixtures of 1- and 2-alkylindazoles are obtained, which are most conveniently separated by fractional distillation followed by crystallisation of the individual fractions, or, when this is not possible, by means of the picrates. The course of the reaction is deduced from a study of the action of ethyl iodide, sodium, and ethyl alcohol on 3-methylindazole, whereby a mixture of 3-methyl-1-ethylindazole, b. p. 245·5° (m. p. of picrate, 190—192° or 192—194°, according to the rate of heating), and 3-methyl-2-ethylindazole, b. p. 284—285° (m. p. of picrate, 212—213°), is obtained, the products being identical with those described by Fischer and Tafel (*loc. cit.*). H. W.

Alkyl Derivatives of Indazole-3-carboxylic Acid. K. VON AUWERS and R. DERESER (*Ber.*, 1919, 52, [B], 1340—1351).—The action of various alkylating agents on indazole-3-carboxylic acid and its esters has been investigated. The behaviour is more complex than that of indazole itself (preceding abstract). Fortunately, the widely differing ease of esterification of the alkylindazolecarboxylic acids affords both a means of fixing their constitution and also of separating mixtures of them into their components. Thus indazole-3-carboxylic acid is readily esterified by the Fischer-Speier process, and this is true of one of the alkylated acids, which is thus a 1-alkyl derivative, whereas the second acid, which can only be esterified with difficulty, must be the 2-alkyl compound. The esters of 2-alkylindazole-3-carboxylic acid are obtained by the action of alkyl iodides on the silver salt of the acid or on the silver compound of the ester.

Direct alkylation of indazole-3-carboxylic acid with alkyl iodide is not a suitable method, since the substances scarcely react at 100°, whilst at higher temperatures compounds containing iodine result. The method may, however, be applied to the esters; thus methyl indazole-3-carboxylate and methyl iodide at 100° yield a mixture of methyl 2-methylindazole-3-carboxylate and the corresponding acid (formed by the action of the liberated hydrogen iodide); the ethyl ester does not react with ethyl iodide under similar conditions.

2-Alkylindazole-3-carboxylic acids are readily obtained by the action of methyl or ethyl sulphate and sodium hydroxide on indazole-3-carboxylic acid, the 1-alkyl isomerides either not being formed at all or in very small amount. The methyl ester, when similarly treated, yields, however, a mixture of the 1- and 2-methyl derivatives. Methyl indazole-3-carboxylate is converted by diazomethane exclusively into the 2-methyl compound.

Alkylation with sodium alkoxide and alkyl iodide leads, in general, to a mixture of isomerides, the relative proportions of

which vary with the particular ester used and also with the alkyl iodide.

The esters of indazole-3-carboxylic acid and its homologues can be distilled without undergoing decomposition, whilst the corresponding free acids eliminate carbon dioxide when heated and yield the indazoles; with the 1-alkyl acids, this happens at the melting point, with the 2-alkyl acids, however, at a higher temperature.

The following individual compounds are described: indazole-3-carboxylic acid, m. p. 260—261°; methyl ester, m. p. 168—169°; ethyl ester, yellow, shining needles, m. p. 136—137°; 2-methylindazole-3-carboxylic acid, m. p. 224—225° (decomp.); methyl ester, yellow crystals, m. p. 61—62°; 2-ethylindazole-3-carboxylic acid, small leaflets, m. p. 180—181°; ethyl ester, slender needles, m. p. 47—48°, b. p. 179—181°/11 mm.; 1-methylindazole-3-carboxylic acid, slender needles, m. p. 213—214°; methyl ester, colourless needles, m. p. 75—77°; 1-ethylindazole-3-carboxylic acid, glassy needles, m. p. 162—163°; ethyl ester, b. p. 190—192°/10 mm.

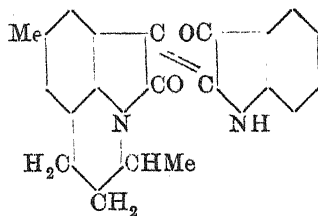
H. W.

The Indirubins. JH. MARTINET (*Compt. rend.*, 1919, 169, 183—185).—The author has prepared a number of substituted indirubins by three different processes, namely, (1) condensation of the isatins with indoxyllic acid in slightly alkaline medium in an atmosphere of hydrogen; (2) condensation of the same isatins with 2-anilinoisatin in ammoniacal solution in a current of hydrogen sulphide; by this method, a large part of the product often remains in the mother liquor as a leuco-base, in which case, after filtration, these liquors should be warmed in a current of air; (3) very easily by adding to an acetic acid solution of the isatin, warmed on a water-bath, the technical fusion of phenylglycine.

The following indirubins have been prepared:

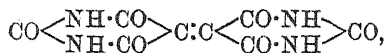
From isatin, indirubin itself; from 1-methylisatin, 2-indoxyl-1-methylindole; from 5-bromo-1-methylisatin, 2-indoxyl-3-(5-bromo-1-methyl)indole, m. p. 265—266°; from 1-ethylisatin, 2-indoxyl-3-(1-ethyl)indole; from 5-bromo-1-ethylisatin, 2-indoxyl-3-(5-bromo-1-ethyl)indole, m. p. 250—251°; from 5-methylisatin, 2-indoxyl-3-(5-methyl)indole, m. p. 289°; from 5:7-dimethylisatin, 2-indoxyl-3-(5:7-dimethyl)indole, m. p. 337°; from 1:7-trimethyleneisatin, 2-indoxyl-3-(1:7-trimethylene)indole, m. p. 252°; from 5-methyl-1:7-trimethyleneisatin, 2-indoxyl-3-(5-methyl-1:7-trimethylene)indole, m. p. 265°; from 5-methyl-1:7- α -methyltrimethyleneisatin, 2-indoxyl-3-(5-methyl-1:7- α -methyltrimethylene)indole (annexed formula), m. p. 204—205°.

All of these substances are obtained as slender, brownish-violet needles. They give violet-red, alcoholic solutions, the colour of which is rapidly removed on warming with a few drops of potassium hydroxide in the case of those indirubins which have a sub-



stituent attached to nitrogen. [See, further, *J. Soc. Chem. Ind.*, September.] W. G.

Hydurilic Acid and s-Dimethylhydurilic Acid. HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1919, 52, [B], 1298—1316).—Hydurilic acid is conveniently prepared by the action of heat on dialuric acid, conversion of the crude product into 5-bromo-5-methoxyhydurilic acid, and reduction of the latter with stannous chloride. It is also readily obtained by oxidation of barbituric acid in aqueous solution with potassium permanganate, but is not formed from an acid solution. Hydurilic acid is itself further oxidised by permanganate, probably to 5-hydroxyhydurilic acid; the product, however, could not be adequately purified, and, further, could not be reduced to hydurilic acid. 5-Methoxyhydurilic acid is readily obtained by the gentle reduction of 5-bromo-5-methoxyhydurilic acid (Biltz, Heyn, and Hamburger, A., 1916, i, 507) by potassium iodide or sodium sulphite, whilst more powerful reducing agents yield hydurilic acid; it forms coarse, hexagonal platelets, which soften at 170° and decompose at 230—240°. With bromine and water, it re-forms bromomethoxyhydurilic acid, whilst with chlorine it gives 5:5'-dichlorohydurilic acid. 5-Ethoxyhydurilic acid, prepared in a similar manner, crystallises in pyramids or double pyramids, which decompose at about 242° after becoming red at about 210°. The alkyloxyhydurilic acids are powerful acids; *potassium methoxyhydurate*, rectangular platelets, is described. The alkyloxy-acids eliminate alcohol when heated, and yield *dehydrohydurilic acid*,



which could not be crystallised without change and which decomposes at about 250°; it appears to be converted in aqueous solution into 5-hydroxyhydurilic acid. The solid acid (but not the aqueous solution) is reduced by potassium iodide to hydurilic acid. With methyl alcohol, chlorine, and bromine, respectively, it yields 5-methoxyhydurilic acid, 5:5'-dichlorohydurilic acid, and 5:5'-dibromohydurilic acid, long, four-sided prisms which evolve bromine at 110° and decompose at 160°. When heated at 120°, the dibromo-acid yields dehydrohydurilic acid, thus exactly resembling 5:5'-dibromotetramethylhydurilic acid; with alcohols, it gives 5-alkyloxyhydurilic acids, whilst dilute aqueous ammonia converts it into 5-aminohydurilic acid, leaflets, decomposing from 70°; the latter is reduced by stannous chloride to uramil and barbituric acid. It reacts with potassium cyanate and molten carbamide, without, however, yielding crystallisable substances. Solid dehydrohydurilic acid also reacts with an aqueous solution of carbamide, giving a *substance*, rectangular platelets, m. p. about 140° (decomp.) after softening at 130°.

5-Methoxy- and 5-ethoxy-tetramethylhydurilic acids are more conveniently prepared by the reduction of 5-bromo-5-methoxy- or

5-bromo-5-ethoxy-tetramethylhydurilic acids with potassium iodide than by the process previously described (*loc. cit.*); tetramethyl-dehydrohydurilic acid readily reacts with chlorine to yield 5:5'-dichlorotetramethylhydurilic acid.

Unsuccessful attempts are described to prepare a monomethyl-hydurilic acid by the action of heat on methylalloxantin; the product, however, was hydurilic acid. Similarly, diethylbarbituric acid was found not to condense with dialuric acid.

[In part, with H. Bülow.]—*s*-Dimethylhydurilic acid, rhombic platelets, which decompose at 306—308° after darkening at 270°, is prepared by heating *s*-dimethylalloxantin at 150°, and is conveniently purified through 5-bromo-5-methoxydimethylhydurilic acid, which decomposes at 235—240° after softening at about 225°. It is converted by methyl sulphate into tetramethylhydurilic acid. 5-Bromo-5'-ethoxydimethylhydurilic acid forms rhombic platelets decomposing at 206—207°. 5-Methoxydimethylhydurilic acid, rectangular platelets, decomposing at 155° after softening at 150°, and 5-ethoxydimethylhydurilic acid, rectangular leaflets, which decompose above 300°, are prepared by the reduction of the corresponding bromo-acids with sodium sulphite. The former, when heated under diminished pressure at 150°, gives crude dimethyl-dehydrohydurilic acid, which, however, could not be purified; on reduction, it yields dimethylhydurilic acid, whilst bromine transforms it into 5:5'-dibromodimethylhydurilic acid, which loses bromine at 80°. 5:5'-Dichlorodimethylhydurilic acid is obtained by the action of hydrochloric acid and potassium chlorate on dimethylhydurilic acid; it forms rhombic platelets, which decompose at 295—300° after becoming discoloured from 270°. H. W.

Formation of Cyanic Acid by Oxidation of Organic Substances. Its Identification Based on Quantitative Analysis. R. FOSSE (*Compt. rend.*, 1919, 169, 91—93).—The presence of cyanic acid in solutions of proteins, alone or with dextrose present, and in ammoniacal solutions of amino-acids, glycerol, carbohydrates, or formaldehyde, after oxidation, is shown by isolating it as its silver salt and analysing this salt. The solution after the oxidation is almost completely neutralised with nitric acid and silver nitrate is added. The precipitate is collected at the pump, washed, and extracted with hot water. On cooling the hot extract, the silver cyanate crystallises out, and may be collected and dried. The salt is heated on a water-bath for one hour in ammoniacal solution with ammonium chloride, after which the solution is acidified with acetic acid and the silver chloride is collected on a Gooch crucible and weighed. The carbamide present in the filtrate is estimated by the usual method. W. G.

Ultramicroscopy of Egg-albumin. J. F. McCLENDON and H. J. PRENDERGAST (*J. Biol. Chem.*, 1919, 38, 549).—A saturated solution of carefully purified crystalline egg-albumin in distilled

water had a p_H about 4.2, and the ultramicroscope showed only an occasional submicron. On bringing it to $p_H=4.8$ and re-examining it by the microscope, there was a slight increase in the number of submicrons. This points to the protein existing in true solution, and it is remarked that it seems unfortunate that clear solutions of protein should be classed with suspensoids under the term "colloids."

J. C. D.

The Nomenclature of Blood Pigment and its Derivatives.

WILLIAM DOBINSON HALLIBURTON and OTTO ROSENHEIM (*Biochem. J.*, 1919, **13**, 195—198).—Attention is drawn to the unsatisfactory system of nomenclature of the blood pigments and their derivatives introduced by Hoppe Seyler. As an entirely new system would confuse the literature, it is suggested that a considerable simplification of that at present in use would be effected by the deletion of the ill-chosen name hæmochromogen. It is pointed out that this substance is without doubt identical with reduced hæmatin (Stokes, *Proc. Roy. Soc.*, 1864, **13**, 353). The substance hitherto termed hæmatin should be called oxyhæmatin. This small change renders it possible to show the relationship of the blood pigments and their derivatives by means of a very simple table.

J. C. D.

The Effect of Alcohol on the Digestion of Fibrin and Caseinogen by Trypsin.

EDWARD STAFFORD EDIE (*Biochem. J.*, 1919, **13**, 219—225).—The action of trypsin on fibrin and on caseinogen is affected by dilute alcohol to such different degrees that it is reasonable to suppose either that there are two enzymes concerned in the digestion of these proteins or that different groups of the same enzyme molecule take part in the hydrolysis of the different proteins.

J. C. D.

Additive Compounds of the Halogen Acids with Diphenylarsinic Acid.

V. GRIGNARD and G. RIVAT (*Compt. rend.*, 1919, **169**, 126—129).—When diphenylarsinic acid is dissolved in hydrochloric acid (D 1.17) and the solution allowed to cool, the hydrochloride, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, m. p. 134° , is obtained, but if the acid is first diluted with two volumes of water, the hydrochloride, $2\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, m. p. 111 — 111.5° , is obtained. The first hydrochloride may be converted into the second by warming it in chloroform with an equimolecular proportion of diphenylarsinic acid, whilst the reverse process is brought about by dissolving the second hydrochloride in hydrochloric acid (D 1.17). In a similar manner, two hydrobromides, the one, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HBr}$, m. p. 126 — 126.5° , the other, $2\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HBr}$, m. p. 119.5 — 120° , have been obtained. The hydrobromides are less stable than the hydrochlorides.

[By CH. MAUGUIN.]—The crystallographic measurements for these addition compounds, all of which crystallise in the monoclinic system, are: the hydrochloride, $\text{AsPh}_2\text{O}\cdot\text{OH}\cdot\text{HCl}$, has $a:b:c=$

0.8063:1:?, $\beta=109^{\circ}25'$; the hydrochloride, $2\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HCl}$, has $\alpha:b:c=0.6346:1:0.801$, $\beta=94^{\circ}30'$; the hydrobromide, $\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HBr}$, has $\alpha:b:c=0.790:1:?$, $\beta=108^{\circ}26'$; the hydrobromide, $2\text{AsPh}_2\text{O}\cdot\text{OH}, \text{HBr}$, has $\alpha:b:c=0.6333:1:0.779$, $\beta=93^{\circ}56'$.

W. G.

Physiological Chemistry.

Relation between the Electric State of the Cell Wall and its Permeability to a Given Ion. PIERRE GIRARD (*Compt. rend.*, 1919, 169, 94—97).—The author has shown that, by modifying the charge on the cell wall in the case of blood corpuscles, its permeability to chlorine ions is also modified. In suspension in 0.9% sodium chloride solution, the corpuscles neither absorb nor emit chlorine, but in a similar solution acidified with lactic acid, taking into account the expansion of the corpuscles, it is shown that chlorine passes in, due to the electrification of the cell wall by the hydrogen ions of the acid. This positive charge induced by the hydrogen ions on the cell walls is partly annulled if the acid used has a high valency, as is shown by replacing the lactic acid with citric acid. The presence in the sodium chloride solution of a non-toxic, alkaline salt, such as potassium carbonate, tends to increase the negative charge on the cell wall, and chlorine, instead of passing into the cell, passes out.

W. G.

Effect of Diet on the Alkaline Reserve of the Blood. J. F. McCLENDON, L. VON MEYSENBUG, O. J. ENGSTRAND, and FRANCES KING (*J. Biol. Chem.*, 1919, 38, 539—548).—The alkaline reserve in man and the dog appears to be very resistant to the influence of the diet. In the case of the rabbit, however, changes due to diet or starvation were noted.

J. C. D.

The Action of Ultraviolet Rays on the Accessory Food Factors. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1919, 13, 164—171).—The accessory food factor present in butter is inactivated by exposure to ultraviolet light for eight hours. This treatment also bleaches the butter and renders it quite unfit for consumption. The antineuritic and antiscorbutic vitamins are not destroyed by ultraviolet rays.

J. C. D.

Relationship of the Pancreatic Enzymes. FREDERIC FENGER and MARY HULL (*J. Biol. Chem.*, 1919, 38, 487—500).—The normal pancreas as removed from the animal is of distinctly acid reaction and possesses high diastatic, considerable lipolytic, and

some proteolytic activity. The first-named enzyme is present in fully activated form, but increased lipolytic activity and proteolytic activity are obtained by the addition of bile and duodenal mucosa respectively. By the addition of adequate amounts of these two substances, it is possible to produce and maintain maximum activity of the three enzymes in the removed pancreas. J. C. D.

The Colours of Colloids. VII. Blue Feathers. WILDER D. BANCROFT (*J. Phys. Chem.*, 1919, **23**, 365—414. Compare this vol., i, 421).—The colours in feathers fall into three categories. Of these, only black, brown, reddish-orange, and yellow are objective chemical colours directly produced by pigment. A second type is structural, notably blue and violet, which are produced by finely divided air bubbles in a specially constructed, transparent layer of thick-walled "box cells" lying below the epidermal cells, which behave in a manner similar to the dust in the atmosphere, and the effect of which is intensified by a brownish-black pigment layer behind. Lastly, there are colours which depend entirely on the position of the light and eye, which are produced by a transparent sheath which acts like a prism. The combination of the structural blue with a yellow pigment gives a structural green. By displacing the air in the "box cells" with a medium of the same refractive index as the cell wall, such as Canada balsam or benzene, the structural blue colour disappears. G. F. M.

The Non-protein Nitrogenous Constituents of Cow's Milk. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **33**, 453—458).—Analyses of the total non-protein nitrogen, amino-nitrogen, urea, uric acid, creatine, and creatinine in cow's milk are given. The content of the first three is influenced by the character of the food, being increased in high protein feeding. High figures for these fractions are also found for colostrum. J. C. D.

The Peroxydases in Milk. H. VIOLE (*Compt. rend.*, 1919, **169**, 248—250).—It is shown from an examination of the mammary glands of guinea-pigs that the peroxydase is contained in the glandular cells, and in the case of a healthy mammal, therefore, not submitted to violent treatment, the fresh milk may contain little or no peroxydase. On the other hand, the milk coming from an animal having any affection of the mammary gland may be rich in peroxydase. Similarly, milk which has been heated at 78—80°, and in which, therefore, the peroxydase has been destroyed, may have the latter restored by the addition of fresh organic tissues or liquids of animal or vegetable origin containing them. The peroxydase test is not therefore trustworthy as a means of distinguishing between fresh and heated milk. W. G.

Mechanism of the Toxic Action of Urease. P. CARNOT and P. GÉRARD (*Compt. rend.*, 1919, **169**, 88—90. Compare *Compt. rend. Soc. Biol.*, 1919, April).—The toxicity of soya flour when

injected intravenously or subcutaneously is shown to be due to the action of the urease present in it. In the case of dogs receiving an intravenous injection, it was found that the carbamide present in the blood disappeared very rapidly, although in some cases it reappeared later. The ammoniacal nitrogen content of the blood and organs increased progressively. The phenomena of cerebral intoxication are due to the localisation of ammonia in the brain, this being produced by the action of the urease on the carbamide of the blood and tissues.

W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Preparation of Silica Jelly for Use as a Bacteriological Medium. ALBERT T. LEGG (*Biochem. J.*, 1919, 13, 107—110).—The success of the method depends on the use of a rather thick collodion dialysing membrane of low permeability, a sufficiently long period being given for the sodium silicate and hydrochloric acid to react after mixing, and the use of distilled water for dialysing. When the product is to be used for culture purposes, it is advisable that tubing and autoclaving should follow immediately after dialysing.

J. C. D.

The Vitamine Requirement of Yeast. A Simple Biological Test for Vitamine. ROGER J. WILLIAMS (*J. Biol. Chem.*, 1919, 38, 465—486).—Attempts to grow pure cultures of yeast in synthetic media from a single cell failed, a finding which recalled the experiments of Pasteur and of Wildiers ("La Cellule," 1901). Further experimentation largely confirmed Wildiers' results, and the possibility of the substance termed "bios" by that author being identical with the water-soluble *B*-vitamine presented itself. It was found that the substance which stimulates the growth of yeast occurs in many of the materials which are known to be sources of water-soluble *B*, and, moreover, the properties of the two substances showed close resemblance. The former substance was not identified as any one of the amino-acids obtained from caseinogen. It is believed that there is justification for concluding that the two substances, Wildiers' "bios" and the so-called water-soluble *B*, are identical.

J. C. D.

Preparation of Glycerol by Fermentation. W. CONNSTEIN and K. LÜDECKE (*Ber.*, 1919, 52, [B], 1385—1391).—The experiments were undertaken with the object of providing the Central Powers with a means of obtaining glycerol after the importation of fats had been prevented by the blockade.

Glycerol is formed to the extent of about 3% in the ordinary

fermentation of sugar, and the yield is considerably increased when fermentation is effected in the presence of slightly alkaline salts, which do not poison the yeast. In these circumstances, however, the solutions are very liable to infection, thereby decreasing the yield of glycerol; in this connexion, sodium sulphite is very useful, since, particularly at high concentrations, it has an antiseptic action and especially hinders the development of the lactic acid bacilli, whilst also it gives the highest yields of glycerol. The latter vary from 23.1% when the weight of sulphite used is 40% of that of the sugar to 36.7% with twice the weight of the sugar; too large an addition of sodium sulphite causes fermentation to be too slow or damages the yeast. The process does not appear to depend on the particular variety of fermentable sugar (refined sugar, crude sugar, or molasses can be used) or on the species of yeast. The latter, which does not increase to more than a slight extent during the sulphite fermentation, can be utilised for further experiments after subjection to a "purification fermentation" in slightly acid solution. The glycerol, after suitable purification, is adapted not only to nitration, but also to pharmaceutical purposes; occasionally it contains small amounts of trimethyleneglycol, probably due to secondary decomposition of glycerol by bacteria.

The volatile products of the fermentation consist chiefly of ethyl alcohol and acetaldehyde. Increase in the quantity of sulphite diminishes the production of alcohol and carbon dioxide and increases that of glycerol and acetaldehyde.

With regard to the mechanism of the reaction, two factors appear to be involved, a general action of salts and a specific sulphite action. Increased production of glycerol occurs in the presence of considerable quantities, not only of slightly alkaline salts, but also of certain neutral or acid salts (calcium chloride, ammonium chloride, sodium chloride, sulphate or nitrate, ferrous sulphate, aluminium sulphate). The specific action of the sulphite is possibly connected with its relationship to aldehydes.

H. W.

The Vegetable Proteases. I. Introductory. ERNEST ARTHUR FISHER (*Biochem. J.*, 1919, **13**, 124—134).—The presence of proteinoclastic and peptoclastic enzymes in a number of green plants (cereals in the grass stage, leguminous plants, buckwheat, and white mustard) has been established. A detailed examination of beans, field peas, and buckwheat indicated that all parts of the plant are active in this respect at all stages of growth. The proteinoclastic and peptoclastic action of the leaves increases with increasing maturity, and does not fall off after the flowering stage. There is a distinct increase in the activity of these enzymes after germination. The suggestion is advanced that the peptoclastic action of green fodder plants is sufficiently great to be of assistance to the animal organism in the digestion of the simple protein substances.

J. C. D.

Organic Chemistry.

Manufacture of Amyl Acetate and its Homologues from Chloro-hydrocarbons of the Paraffin Series. G. G. OBERFELL and H. T. BOYD (U.S. Pat. 1302583; from *J. Soc. Chem. Ind.*, 1919, **38**, 554A).—Chloro-paraffins are converted into acetic esters by treatment with an alkali acetate and acetic acid in presence of an alkali sulphate. G. F. M.

The Insecticidal Principle of *Chrysanthemum cinerarii-folium* (Insect Powder). RYŌ YAMAMOTO (*Ber. Ōhara Inst. landw. Forsch.*, 1918, **1**, 389—398).—A yellow, viscous oil having powerful insecticidal properties was isolated from the powdered flowers of *Chrysanthemum cinerarii-folium*, the yield being 0.8%. The oil had a saponification number of 216 and an iodine number of 116; from the saponified substance, two alcohols having the formulæ $C_{21}H_{44}O$, m. p. 199° , and $C_{27}H_{56}O$, m. p. $175-179^{\circ}$, and two fatty acids having the formulæ $C_{10}H_{18}O_2$ and $C_{16}H_{32}O_2$ (palmitic), were separated. The insecticidal power of the oil was reduced when the oil was heated at 100° or exposed to air for a long period. W. P. S.

Action of Methyl Sulphate and Methyl Alkali Sulphate on Dry Alkali Chlorides and Bromides. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 435—437).—When methyl sulphate is heated with sodium chloride, reaction at first appears to take place according to the equation $Me_2SO_4 + NaCl = NaMeSO_4 + MeCl$, and is followed by a reaction shown by the equation $2NaMeSO_4 = Na_2S_2O_7 + OMe_2$. The residue, however, always contains normal sodium sulphate, and the quantities of the two gases formed are not theoretical; methyl chloride is in excess. If equimolecular quantities of methyl sulphate and potassium chloride are heated together, two-thirds of the methyl sulphate reacts according to the second of the above equations, the remainder reacting with the potassium chloride, $KMeSO_4 + KCl = K_2SO_4 + MeCl$. If two molecules of potassium chloride are used, the latter reaction disappears almost completely, and the reaction is represented by the equation $2Me_2SO_4 + 2KCl = 2MeCl + OMe_2 + K_2S_2O_7$. Bromides behave in a similar way to chlorides in the reactions. W. P. S.

Interaction between Methyl Sulphate and Chloro-sulphonic Acid. CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 338—341).—Equimolecular proportions of methyl sulphate and chlorosulphonic acid slowly react according to the equation $SO_2(OMe)_2 + SO_2Cl \cdot OH \rightleftharpoons SO_2Cl \cdot OMe + SO_2(OH) \cdot OMe$,

an equilibrium being reached at the end of a month, when the reaction has proceeded to the extent of 36% to the right. If kept for a further period, a change in acidity slowly occurs, owing to the formation of sulphuric acid, according to the equation $\text{SO}_2(\text{OH})\cdot\text{OMe} + \text{SO}_2\text{Cl}\cdot\text{OH} \rightleftharpoons \text{SO}_2\text{Cl}\cdot\text{OMe} + \text{H}_2\text{SO}_4$; this change at the end of 138 days has not quite reached equilibrium. When, on the other hand, the reaction mixture is subjected to vacuum distillation, the two initial materials practically disappear, and a yield of 50% of methyl chlorosulphonate is obtained, together with small quantities of hydrogen chloride, methyl chloride, and a residue of sulphuric acid. G. F. M.

Wax of a South Brazilian Wild Bee. J. GADAMER (*Arch. Pharm.*, 1917, **255**, 425—441).—The characters and composition of wax produced by a wild bee, probably of the species *Melipona* or *Trigona*, are described. [See *J. Soc. Chem. Ind.*, 1919, 730A.] T. H. P.

Lipoids of the Heart Muscle. P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, **39**, 83—89).—The analysis of the so-called lecithin fraction obtained from heart muscle demonstrates that this fraction is a mixture of lecithin and kephalin. When reduced by means of hydrogen in the presence of colloidal palladium, a product was obtained having all the properties of the crude hydrolecithin obtained from egg-yolk (Levene and West, A., 1918, i, 288, 421). From this mixture, by fractionation, hydrolecithin and hydrokephalin were isolated.

The opinion expressed by Fränkel and Linnert (A., 1910, i, 295) that individual organs of the same animal contain specific phosphatides appears to lack support. There is rather an indication that the number of individual lipoids is limited, and that practically all animal organs contain the same lipoids. J. C. D.

Kephalin. VI. The Bearing of Cuorin on the Structure of Kephalin. P. A. LEVENE and S. KOMATSU (*J. Biol. Chem.*, 1919, **39**, 91—104).—The components of kephalin hitherto isolated are phosphoric acid, glycerol, aminoethyl alcohol, and stearic and linoleic acids. A molecule composed of equimolecular proportions of these would demand a different percentage composition from that usually found. The discrepancy could be explained on one of three grounds: first, that kephalin possesses a structure different from the one expressed by the above method; secondly, that kephalin isolated by the usual methods represented a substance modified in the course of preparation; and thirdly, that a substance of unknown composition was present as an impurity. The recent work of Levene and West (A., 1918, i, 421) on the preparation of a reduced kephalin possessing an elementary composition required by a molecule constituted as above excludes the first of the three alternatives. The work recorded in this paper shows that kephalin as usually prepared is a mixture of true kephalin with its own decomposition products. This explains the widely different

analytical data recorded by previous workers. One of the decomposition products is kephalin from which one fatty acid has been removed either by chemical manipulation or by enzymes. Substances were also obtained which consisted of products of deeper deterioration than the loss of one acid molecule. This conclusion was arrived at in the course of an investigation into the chemical nature of cuorin.

Support is given to the view of Maclean ("The Lipins," London, 1918, 52), who doubted that cuorin is an individual substance. The greater part of cuorin is made up of crude kephalin.

J. C. D.

Preparation of Monochloroacetic Acid. L. J. SIMON and G. CHAVANNE (U.S. Pat. 1304108; from *J. Soc. Chem. Ind.*, 1919, 38, 553A).—Monochloroacetic acid is prepared by heating trichloroethylene with sulphuric acid containing a small amount of water.

G. F. M.

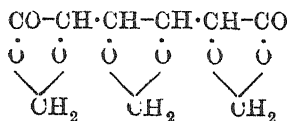
Oxidation of Lactic Acid by Bacteria with Formation of Pyruvic Acid and Ketonic Substances. P. MAZÉ (*Compt. rend. Soc. biol.*, 1918, 81, 1150—1152; from *Chem. Zentr.*, 1919, i, 960).—The author has isolated a dozen types of bacteria which have the power of forming pyruvic acid and ketonic substances by the oxidation of lactic acid in a purely mineral nutrient solution and with calcium lactate as the sole source of carbon. The same types also produce pyruvic acid from similar solutions containing sugar, from which they form lactic acid; only in one instance does the alcoholic fermentation of sugar also occur. The course of the action has been more closely studied with six varieties, the pyruvic acid being estimated colorimetrically by Simon's reaction; for this purpose, the content of the solution must lie between 0.1 and 1%. Formation and decomposition of pyruvic acid occur at different rates with the various species. The yield of acetic acid varies from traces to more than 50% of the lactic acid decomposed, but formic acid is never produced. Two species produce, further, acetylmethylcarbinol and dimethyl diketone, whilst one species produces the latter only. The processes involved are indicated by the equations $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{COMe} + 2\text{CO}_2 + \text{H}_2\text{O}$ and $2\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{H} + \text{O} = \text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3 + 2\text{CO}_2 + \text{H}_2\text{O}$. Dimethyl diketone might possibly be formed by direct oxidation of the secondary alcoholic group of acetylmethylcarbinol, but the complete absence of butylene glycol renders this improbable.

H. W.

Quantitative Studies on the Succinic Oxidone of Battelli and Stern. HANS EINBECK (*Biochem. Zeitsch.*, 1919, 95, 296—305. Compare Battelli and Stern, A., 1913, i, 929).—It appears probable that two quite distinct processes may take place when succinic acid is acted on by muscle pulp in the presence of oxygen. First, there is the elimination of two atoms of hydrogen with the formation of fumaric acid. This reaction is quantitative,

the amount of oxygen required being proportional to the amount of succinic acid in the reaction mixture. Then there is the addition of a molecule of water at the unsaturated linking of the fumaric acid, with the formation of *i*-malic acid. This reaction is not quantitative, but tends to an equilibrium, at which approximately a quarter of the fumaric acid remains unchanged. J. C. D.

Behaviour of the Methylene Group United to the Carboxyl Group in Trimethylenesaccharic Acid. CESARE PADERI (*Arch. farm. sper. sci. aff.*, 1918, 26, 274—282; from *Chem. Zentr.*, 1919, iii, 65).—Opportunity is afforded by trimethylenesaccharic acid (annexed formula) of further investigation



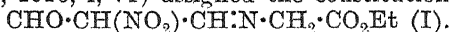
of the author's views on the relative stability of methyl groups which esterify hydroxy-groups or hydroxy- and carboxyl groups respectively (compare A., 1917, i, 716). The acid is hydrolysed by boiling water containing a small quantity of sulphuric acid to monomethylenesaccharic acid and formaldehyde. A similar fission appears to occur in the rabbit, since formaldehyde can be detected in the urine after administration of the acid. H. W.

Linoleic Acid and its Derivatives. KATSUMI TAKAHASHI (*J. Tokyo Chem. Soc.*, 1919, 40, 233—289).—Linoleic acid can be estimated only by converting it into its derivatives. Physical and chemical properties, however, of both the bromo- and hydroxy-derivatives into which linoleic acid is ordinarily converted are confusing according to the different authors (compare Reformatzky, A., 1890, 362). Furthermore, the value obtained by the tetrabromostearic acid method is invariably less than that calculated from the iodine number in the presence of another unsaturated fatty acid. In order to investigate the source of this discrepancy, the author made extensive studies of the properties of various derivatives of linoleic acid. Linoleic acid is first separated by brominating linoleic acid from oil of rice bran and soja bean. This tetrabromostearic acid, which he designates as (A)-bromo-derivative, after repeated crystallisation from light petroleum, forms white, needle-shaped crystals, m. p. 114°. It is soluble in ether, but insoluble in light petroleum at the ordinary temperature. When converted into the methyl ester by Rollett's method, and hydrolysed to linoleic acid, a 90% yield calculated on the basis of the (A)-bromo-derivative, or 97% if calculated on the basis of its methyl ester, was obtained. An analysis shows its composition to be exactly that of linoleic acid. When this is again brominated, it yields three types of bromo-derivatives, regardless of the kinds of solvent used: (α) m. p. 113.5—114°, containing 53.38% of Br, insoluble in light petroleum; (β) m. p. 59—60°, containing 53.35% of Br, soluble in light petroleum; (γ) liquid, containing 52.86% of Br, soluble in light petroleum. Since the theoretical value for

tetrabromostearic acid, $C_{18}H_{32}O_2Br_4$, is 53.33% of Br, he concludes all these three varieties of bromo-derivatives must be tetrabromostearic acid. The yields of the three derivatives vary somewhat with the types of solvent used. With light petroleum as solvent, 43—46% of the total yield is in the α -form, the remaining 49.2% to 52.66% being β and γ ; with carbon tetrachloride, 39% α and 56% β and γ ; with ethyl ether, 47% α , 51.77% of β and γ ; with glacial acetic acid, 35% of α . In all cases, the α -form, which possesses exactly the same physical properties as the parent compound (that is, tetrabromostearic acid, m. p. 114° , soluble in light petroleum), is obtained only in a quantity of 49% of the (A)-bromo-derivative, the remaining portion being the same tetrabromostearic acid but having entirely different physical properties. When the α -variety is again reduced to linoleic acid and brominated for a third time, it gives 42.4—46% of the α -form and 52.8—55.8% of β and γ . From the β -form, 36.7% of the α , 48% of β , and 22.4% of γ ; from the γ -form, 24—26% of α , 8.05—8.4% of β , but 67.95—65.35% of γ are obtained. In general, all three racemic varieties of tetrabromostearic acid can be reduced to linoleic acid, and on further bromination each yields three varieties of bromo-derivatives, always, however, giving most of its own kind. The oxidation products of linoleic acid obtained from the α - and β -forms are a large quantity of sativic acid, m. p. 174° , and a small quantity of another tetrahydroxystearic acid, m. p. 135° . The linoleic acid obtained from the γ -form yields neither sativic acid nor the other tetrahydroxystearic acid, but gives an acid, $C_{16}H_{31}O_2\cdot OH$, soluble in water and a rosin-like substance insoluble in water and having the formula $(C_8H_8O_2)_n$. By applying the same method to the natural linoleic acid in the presence of unsaturated fatty acids, only 40% of the original amount of linoleic acid is obtained as the crystallised tetrabromostearic acid insoluble in light petroleum. The author proposes, therefore, a factor 2.5 to be used for linoleic acid estimations if it is to be isolated as the insoluble tetrabromostearic acid. Several analytical data are given to show that this factor is most satisfactory.

CHEMICAL ABSTRACTS.

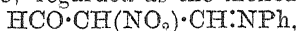
Condensation of Amino-compounds with Nitromalon-aldehyde. WILLIAM J. HALE and EDWARD M. HONAN (*J. Amer. Chem. Soc.*, 1919, **41**, 770—776).—To the aldehydic intermediate product formed in the preparation of carbopyrrolic esters by the condensation of aminoacetic esters with nitromalon-aldehyde, Hale and Hoyt (A., 1916, i, 71) assigned the constitution



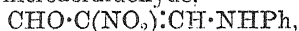
It is now found that such intermediate product is capable of formation in dilute alkaline solution, from which it separates readily. The substance separating is not, however, a salt, and is transformed by warm alkali into a pyrrole derivative, which the Hinsberg reaction and the Liebermann nitrosoamine reaction show to be a secondary amine. This intermediate compound must therefore have the constitution $CHO\cdot C(NO_2):CH\cdot NH\cdot CH_2\cdot CO_2Et$, the

isonitro-compound (I) first produced undergoing intramolecular rearrangement with transfer of the labile hydrogen atom from the central carbon to the nitrogen.

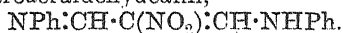
The assumption that the intermediate compound possessed the structure (I) was based on the results of Hill and Torrey (A., 1899, i, 788), who ascribed similar constitutions to a number of products resulting from the condensation of nitromalonaldehyde with amino-derivatives. With aniline, these authors obtained two compounds which they regarded as the monoanil,



and the dianil, $\text{NPh}\cdot\text{CH}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}\cdot\text{NPh}$; neither of these compounds exhibits any tendency to form salts, and as they are now found to be secondary amines, they must be regarded respectively as β -anilino- α -nitroacraldehyde,

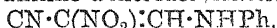


and β -anilino- α -nitroacraldehydeanil,



The similar compounds furnished by *p*-toluidine and by methylamine and its derivatives must receive analogous formulæ.

The action of 1 mol. of hydroxylamine on nitromalonaldehyde gives an unstable compound which immediately undergoes intramolecular condensation to a β -nitroisooxazole, whereas excess of hydroxylamine gives a dioxime stable in alkaline solution. The action of aniline hydrochloride on the sodium salt of this dioxime precipitates Hill and Hale's anil-oxime (A., 1903, i, 401), which is formed also by the interaction of hydroxylamine and the so-called monoanil (see above), and must therefore be a β -anilino- α -nitroacraldioxime, $\text{NOH}\cdot\text{CH}\cdot\text{C}(\text{NO}_2)\cdot\text{CH}\cdot\text{NHPh}$; dehydration of this oxime gives a β -anilino- α -nitroacrylonitrile,



which Hill and Hale termed a nitrile-anil.

These facts render necessary a modification of Hale and Hoyt's interpretation (*loc. cit.*) of the condensation of nitromalonaldehyde with glycine ester; no rearrangement in the pyrrole molecule is necessary for condensation after the intramolecular rearrangement of compound (I).

The condensation of nitromalonaldehyde with β -alanine ethyl ester proceeds easily in slightly alkaline solution or in presence of sodium acetate. β -(β -carbethoxyethylamino)- α -nitroacraldehyde being formed. Further intramolecular condensation sufficient to render possible the isolation of a pyrrole could not be effected, the only indication of the formation of a pyrrole derivative being the reddening of a pine splinter held in the vapour produced when the compound was heated with concentrated hydrochloric acid.

The results obtained lead to the conclusion that, in aliphatic imino-compounds presenting an aldehyde group in such position that its possible inter-reaction with a methylene group adjacent to the imino-group may lead to a pyrrole, this condensation is highly favoured when the methylene group is attached to a carbethoxyl or other negative component. If, however, the carbethoxyl group

is once removed from the particular methylene group by the interposition of another methylene group, the influence of the carbethoxyl group becomes so slight that neither the first nor the second methylene group exhibits any marked tendency to condense with the aldehyde group.

α-Nitro-β-(β-carbethoxyethylamino)acraldehyde,
 $\text{CHO} \cdot \text{C}(\text{NO}_2) : \text{CH} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$,

forms colourless prisms, m. p. 79° , and gives various reactions for aldehydes and also Liebermann's nitrosoamine reaction.

α-Nitro-β-(β-carbomethoxyethylamino)acraldehyde,
 $\text{NO}_2 \cdot \text{C}_5\text{H}_7\text{O} \cdot \text{CO}_2\text{Me}$,

forms colourless leaflets, m. p. 66° , and gives the same reactions as the preceding compound.

T. H. P.

Thiocyanoacetone and its Derivatives and Isomerides.

JOSEPH TCHERNIAC (T., 1919, 115, 1071—1090).

Photosynthesis of Formaldehyde and Sugar. P. R. KÖGEL (*Biochem. Zeitsch.*, 1919, 95, 313—316).—A theoretical consideration, in which changes of the keto-enol type are held to be of importance in the photosynthesis of formaldehyde and sugar.

J. C. D.

Degradation of Sugars by Enzymes. H. VON EULER and O. SVANBERG (*Zeitsch. physiol. Chem.*, 1919, 105, 187—239).—The course of the fermentation of sugars by a top yeast and a torula in an alkaline medium ($p_{\text{H}}=8$) has been studied. Under these conditions, alcohol and carbon dioxide are produced in equivalent amounts representing, for both products, 30—33% of the fermented sugar. Dextrose and laevulose, as well as invert-sugar, are rapidly fermented at $p_{\text{H}}=8$, but mannose and galactose are less readily attacked. Sucrose is fermented as rapidly as dextrose at this degree of alkalinity, but maltose remains untouched. These observations indicate that invertase is active at $p_{\text{H}}=8$, but that maltase is not. The inversion of sucrose was quantitatively studied as far as $p_{\text{H}}=8.5$ by repressing the fermentation by means of additions of toluene. The influence of a number of poisons on the fermentation in an alkaline medium is described. More or less marked inhibition was caused by chloroform, toluene, acetaldehyde, aniline, pyridine, resorcinol, sodium picrate, and phenol. Sodium salicylate caused a slightly increased rate of fermentation, whilst sodium lactate, chloroacetic acid, adrenaline, thyroid extract, and sodium thiosulphate had no appreciable effect. Drying at the ordinary temperature did not affect the activity of a yeast at $p_{\text{H}}=8$. The growth of yeasts in alkaline solutions has also been investigated.

J. C. D.

Occurrence of Difficultly Reducing Carbohydrates in Urine. RAGNAR BERG (*Deut. Med. Woch.*, 1919, 45, 435—436; from *Chem. Zentr.*, 1919, iii, 33).—It has long been known that certain urines which do not contain dextrose have the

power of reducing copper sulphate; the solution becomes milky, and finally, particularly when preserved, a yellow, more or less heavy, flocculent precipitate separates which differs completely from the heavy, red precipitate produced by sugar. The author has been able to isolate the difficultly reducing sugar, which appears to be identical with Leo's sugar, in the form of colourless needles, about 2 mm. in length. It is found that urine (in the presence or absence of sugar), which gives the characteristic reaction after fermentation, also exhibits levorotation. The reaction is frequently observed in cases of diabetes and neurasthenia, and particularly of gout. The author therefore designates the substance *arthritose*.
H. W.

Chitose. WALTHER ARMBRECHT (*Biochem. Zeitsch.*, 1919, **95**, 108—123).—Chitosan is completely dissolved by the action of nitrous acid. The solution contains carbohydrates of more than one type, but no crystalline sugar could be isolated. A crystalline osazone, m. p. 202°, was isolated from this mixture. This product is apparently identical with the osazone of chitose. From the products obtained by oxidising the crude "chitose syrup" with nitric acid, a monocarboxylic acid was obtained, which forms a cinchonine salt, colourless prisms, m. p. 200°, and may possibly contain a hydrofuran ring.
J. C. D.

Epifucose. E. VOTOČEK and J. ČERVENÝ (*Zeitsch. Zuckerind. Böhm.*, 1917, **42**, 215—217).—Fuconic acid is converted into epifuconic acid by treatment with pyridine and water, and the lactone of the latter acid is reduced by sodium amalgam to *epifucose*, which was isolated as a sweet, viscous, pale yellow syrup, and did not crystallise even after preservation during six months; it has $[\alpha]_D$ ca -9°. The phenylosazone, m. p. 177—178° (decomp.), and the *p*-bromophenylosazone, m. p. 204°, are identical with the products obtained from fucose.
H. W.

Plant Colloids. VII. Diastase Action. M. SAMEC (*Koll. Chem. Beihefte*, 1919, **10**, 289—304. Compare A., 1914, i, 930; 1915, i, 941).—The processes occurring in the diastatic fermentation of starch have been investigated in the following manner: 10 grams of potato starch were heated with 900 c.c. of water at 120° for half an hour, then cooled to 50° and kept at this temperature, 100 c.c. of 1% diastase solution added, and the reaction allowed to proceed at 50°. At measured intervals of time, 25 c.c. of the reaction mixture were removed and heated rapidly to 100° to stop the action, and then cooled to 25°, at which temperature it was examined. The samples were measured to find, respectively, (i) the molecular weight of the non-dialysable fraction of the products of hydrolysis, that is, the portion with molecular weight greater than 2000—the freezing-point method was used for this purpose; (ii) the colour produced with iodine; (iii) the optical rotation; (iv) the reducing action on Fehling's solution; (v) the

specific conductivity; (vi) the hydrogen-ion concentration; (vii) the velocity of cataphoresis; and (viii) the content of phosphoric acid. The whole of these factors were plotted against the time during which the reaction had been proceeding, and from the curves produced, the following mechanism of the process is deduced. Under the influence of the ferment, the starch molecule decomposes into at least two unequal parts. Of these, one is very like starch in its properties; the other (dialysable) has a somewhat similar structure, since it colours iodine blue. The constitution of the starches and the dextrans appears to be almost analogous, since the optical rotation of both is very similar. The dialysable product possesses marked reducing properties. As the reaction proceeds, the colloidal starch residue separates products of high molecular weight which are more easily dialysable and give a blue iodine reaction. When the molecular weight of the colloidal residue has sunk to below 20,000, the dextrin molecules which separate give a red iodine reaction, and as the process continues they do not give an iodine reaction at all. The initial dextrin products are further decomposed, forming erythro-dextrans and sugar, and the erythro-dextrans pass over into achroo-dextrans. A tabulated scheme of the process, giving molecular weight and iodine reaction at the various stages of the process, is included in the paper.

J. F. S.

The Acetyl Content of Lignin. HANS PRINGSHEIM and HANS MAGNUS (*Zeitsch. physiol. Chem.*, 1919, 105, 179—186).—The author has investigated the origin of the acetic acid produced in the dry distillation of wood and in the processes by which wood and straw are broken down by digestion with alkali. In the latter process, the whole of the acetic acid formed is derived from the lignin substance when the digestion is carried out without heating. If, however, the wood or straw is treated with a solution of sodium hydroxide at the b. p., with or without the use of increased pressure, a small fraction of the acetic acid formed has its origin in cellulose.

The lignin prepared according to the method of Willstätter and Zechmeister (*Zeitsch. angew. Chem.*, 1919, 32, 41) is not identical with the natural product, since it has undergone hydrolysis and lost its acetyl groups. The natural product may be regenerated by acetylation. The lignin from hornbeam contains nearly double the number of acetyl groups found in lignin from pine-wood.

J. C. D.

Sulphite Liquors. KARL H. A. MELANDER (*Tekn. Tidskr.*, 1918, 10—12, pp. 36; from *Chem. Zentr.*, 1919, i, 862—863).—By treatment of sulphite liquor with sodium chloride, the author has obtained a substance which differs considerably in its properties from that prepared by Klason by precipitation with calcium chloride; after purification, it forms a mixture of similar ligninsulphonic acids of high molecular weight in

u*

which a portion of the sulphur dioxide is loosely held in ester-like combination. The author designates the mixture *α-lignin-S-acid*, and has shown that the main portion of it is monobasic, whilst only a small part is dibasic. Vanillic acid, protocatechuic acid, and catechol are formed when it is fused with alkali under various conditions. Acetic acid and small amounts of higher fatty acids are also produced, thus pointing to the presence of acetyl groups. The yield of catechol attains 10% of the organic matter of the original substance. Free *α-lignin-S-acid* is obtained as a pale brown powder, which readily becomes resinified when hydrochloric acid is added to the solution of the salted-out product. It is hydrolysed by treatment with alkali. There appears to be little prospect of obtaining the acid in the crystalline condition, since analyses indicate that it is a mixture of relatively complex compounds of almost identical percentage composition. In the *salts* with naphthylamine and toluidine, an atom of nitrogen is present for each atom of sulphur; the latter, however, appears to be present in different forms, partly firmly and partly loosely combined, in the acid. The *sodium* salt is described. The brown colour of *α-lignin-S-acid* renders its titration in the presence of indicators a matter of difficulty. The equivalent, 782, is obtained by titration with sodium hydroxide and determination of the end-point by measurement of the electrolytic conductivity of the solution. Comparison of the potential of the solution against that of a calomel electrode gave the value 882 for another specimen. In certain cases, the use of phenolphthalein was also found possible, and the results show that the presence of an atom of sulphur in the free acid corresponds with that of one ionisable hydrogen atom, so that a carboxyl group cannot be present. The sodium salt is not perceptibly hydrolysed; determinations of the molecular weight in aqueous solution by the freezing-point method gave values between 822 and 991 for different specimens. The electrolytic conductivity of aqueous solutions of the sodium salt at different dilutions has also been determined.

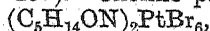
H. W.

Preparation of Butylamine and of *n*-Dibutylamine. The Separation of Aliphatic Amines by Partial Neutralisation. EMIL ALPHEONSE WERNER (T., 1919, 115, 1010—1014).

Biochemical Formation of Aminoethyl Alcohol from Serine. F. F. NORD (*Biochem. Zeitsch.*, 1919, 95, 281—285).—Aminoethyl alcohol was isolated from the products of the decomposition of serine by putrefactive bacteria. Ten grams of the amino-acid yielded 2·8 grams of crude aminoethyl alcohol picrolonate.

J. C. D.

The Muscarine Question. I. Double Salts of certain Bases with Platinum. ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1919, 105, 249—257).—Choline platinibromide,



large, dark red prisms or octahedra, m. p. 240° (decomp.), is sparingly soluble in cold water. Choline hydrobromide gives a

dark red precipitate with chloroplatinic acid. This double salt crystallises from water in prisms and plates, m. p. 255° (decomp.). It is apparently the compound $(C_5H_{14}ON)_2PtClBr_5$. Betaine platinibromide crystallises from water in dark red four- or six-sided prisms which decompose at 240° . Pyridine platinibromide, $(C_5H_5N)_2 \cdot H_2PtBr_6$, dark red, short prisms, decomposes at about 280° . On heating the aqueous solution of this salt, a finely crystalline, golden-yellow double salt separates, $(C_5H_5N)_2PtBr_4$, which chars at about 150° . In the course of this change, an intermediate product, $[Pt(C_5H_5N)Br_5]HC_5H_5N$ (?), was isolated.

Arecaidine platinibromide, $(C_7H_{11}O_2N)_2 \cdot H_2PtBr_6 \cdot H_2O$, forms dark red, eight-sided prisms, and also cinnabar-red, thin, rhombic plates, decomp. 238° . If a solution containing arecoline hydrobromide and chloroplatinic acid is warmed, it turns dark red, and a dark red double salt crystallising in six-sided plates and short prisms separates. This is apparently $(C_8H_{13}O_2N)_2 \cdot H_2PtCl_2Br_4$.

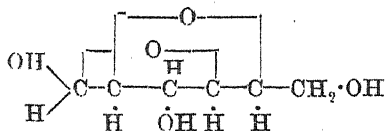
Nicotine platinibromide, $C_{10}H_{14}N_2 \cdot H_2PtBr_6 \cdot H_2O$, minute, dark red crystals, decomposes at 230° . It is decomposed by water with formation of an orange-yellow product.

No double salts were isolated and identified in the case of morphine and hydrazine.

J. C. D.

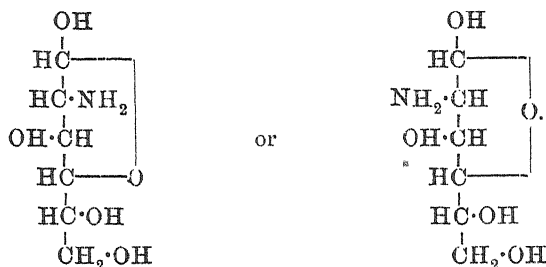
Epichitosamine and Epichitose. P. A. LEVENE (*J. Biol. Chem.*, 1919, **39**, 69—76).—The synthesis of epichitosamine is given. This sugar and chitosamine constitute the first pair of epimeric hexosamines. By reduction of the lactone hydrochloride with sodium amalgam, the crystalline epichitosamine, $C_6H_{13}O_5N$, was obtained (hydrochloride, $C_6H_{13}O_5N \cdot HCl$, m. p. 187° [corr.], $[\alpha]_D^{20} - 4.7^{\circ}$). The osazone has m. p. 205° , and the rotation is in accord with that found for glucosazone. Efforts to obtain the monocarboxylic acid failed, but on oxidation of the hydrochloride with nitric acid, saccharic acid was formed. From the hydrochloride, by the action of mercuric oxide, the sugar epichitose, m. p. 240° (corr.) (decomp.), $[\alpha]_D^{25} - 96^{\circ}$, was prepared in a crystalline condition. It reduces Fehling's solution.

Epichitosamine and epichitose show no mutarotation. If, in the former case, this is ascribed to the presence of the betaine structure assumed by Irvine and Hynd (T., 1912, **101**, 1136), it would be expected that it would react differently from the other amino-sugars with nitrous acid. No such difference could, however, be detected. Attempts to oxidise the sugar failed. Another peculiarity of the sugar lay in its behaviour towards mercuric oxide. Whilst other sugars under this treatment were transformed into the corresponding amino-acids, epiglucosamine formed epichitose. Epichitose may be represented graphically:



A further peculiarity of epichitosamine was found in its behaviour towards nitrous acid. In this case, saccharic acid was obtained, and no dehydration with ring formation followed deamination.

Epichitosamine appears to be an α -amino-sugar, and there are reasons for believing that it is represented by one of the following formulæ:



J. C. D.

d-Chondrosamino- and *d*-Chitosamino-heptonic Acids.

P. A. LEVENE and I. MATSUO (*J. Biol. Chem.*, 1919, **39**, 105—118. Compare Levene, A., 1916, i, 203, 712).—The present communication contains specific directions leading to satisfactory yields of chondrosaminoheptonic acid, and simplified directions for the preparation of chitosaminoheptonic acid. By the action of hydrocyanic acid on hexosamines, a mixture of the two epimerides is obtained. The *d*-chondrosaminoheptonic acids had $[\alpha]_D^{25} - 3.5^\circ$. By fractional crystallisation, a levorotatory *d*-chondrosaminoheptonic acid, elongated prisms, m. p. 139° (corr.) (decomp.), and a dextrorotatory *d*-chondrosaminoheptonic acid, were separated. The former showed an original rotation, $[\alpha]_D^{20} - 8.25^\circ$, and an equilibrium value of $[\alpha]_D^{25} - 13.00^\circ$. This form predominated in the original mixture. *d*-*d*-Chondrosaminoheptonic acid has an initial rotation $[\alpha]_D^{25} + 42.5^\circ$ and an equilibrium rotation $[\alpha]_D^{25} + 65.0^\circ$. The *d*-chitosaminoheptonic acids with original rotation $[\alpha]_D^{20} + 4.0^\circ$ and equilibrium rotation $[\alpha]_D^{20} - 1.0^\circ$ were separated into a dextrorotatory *d*-chitosaminoheptonic acid, heavy prisms, m. p. 192° (decomp.), initial rotation $[\alpha]_D^{25} + 6.5^\circ$ and equilibrium rotation $[\alpha]_D^{25} + 2.75^\circ$, and a levorotatory *d*-chitosaminoheptonic acid, prismatic needles, m. p. 139° (corr.) (decomp.), initial rotation $[\alpha]_D^{25} - 7.5^\circ$ and equilibrium value $[\alpha]_D^{25} - 12.0^\circ$. In the original mixture, the dextro-form predominates.

The attempt to isolate the deaminised heptonic acids in a satisfactory condition failed.

After oxidation with nitric acid after deamination, insoluble calcium salts were obtained, which on analysis appeared to be the calcium salts of trihydroxyglutaric acids. The calcium salts obtained from the two acids showed different optical rotation; that from chondrosaminoheptonic acid had $[\alpha]_D^{25} + 5.0^\circ$ (initial) and $[\alpha]_D^{25} + 1.5^\circ$ (equilibrium), whilst that from chitosamino-

heptonic acid had $[\alpha]_D^{25} + 10.0^\circ$ (initial) and $[\alpha]_D^{25} + 17.0^\circ$ (equilibrium). Theoretically, both aminoheptonic acids should yield the same trihydroxyglutaric acid. J. C. D.

Constitution of Carbamides. IX. The Interaction of Nitrous Acid and Mono-substituted Ureas. The Preparation of Diazomethane, Diazoethane, Diazo-*n*-butane, and Diazoisopentane from the Respective Nitrosoureas. EMIL ALPHONSE WERNER (T., 1919, 115, 1093—1102).

Cyanogen Chloride. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, 169, 474—476).—There are only two cyanogen chlorides. One, a volatile liquid, has the following constants: m. p. -6.5° , b. p. $+12.5^\circ/760$ mm., D_0 1.222, mean coefficient of expansion ($0-45^\circ$) 0.0019. The other chloride is a solid polymeride, m. p. 145° . The volatile chloride is prepared by the action of chlorine or an acidified solution of sodium hypochlorite on aqueous solutions of hydrogen cyanide, or of equimolecular proportions of sodium cyanide and hydrogen chloride. It is conveniently obtained by the electrolysis of solutions containing equimolecular proportions of hydrogen cyanide and chloride, using a graphite anode in a closed porous pot provided with a delivery tube leading to a freezing bath for the collection of the cyanogen chloride. The porous pot stands in a metal vessel, serving as the cathode, and containing dilute hydrochloric acid. The yield varies from 75 to 80% of the theory. The optimum concentration of the solutions is about 2 gram-mols. per litre, and under these conditions no appreciable hydrolysis of cyanogen chloride by the aqueous hydrochloric acid occurs. The method of Sérullas, namely, the action of chlorine on mercuric cyanide, gives precisely the same product as that obtained by the other methods. G. F. M.

α -, β - and γ -Trinitrotoluenes. HUGH RYAN and W. M. O'RIORDAN (*Proc. Roy. Irish Acad.*, 1918, 34, 175—193).—The sensitive product to the presence of which accidents with α -trinitrotoluene are attributed is usually regarded as derived from α -trinitrotoluene itself, but the assumption that it is derived from the β - or γ -isomeride is equally probable, and would be the more likely if the latter compounds were chemically more reactive than the α -compound. The behaviour of the three isomerides towards alkalis, amines, hydrocarbons, and aldehydes under comparable conditions has therefore been investigated, and also that of *s*-trinitrobenzene towards alkalis.

The action of aqueous alkali on *s*-trinitrobenzene yields (1) tetranitroazoxybenzene (compare Lobry de Bruyn, A., 1895, i, 653), which exhibits reactions similar to those of Anschütz and Zimmermann's tetranitroazoxytoluene; (2) a small proportion of a compound, m. p. $200-220^\circ$, which is possibly hexanitrodiphenyl (m. p. 234°).

With sodium *n*-butoxide, α -trinitrotoluene gives a moderately stable compound, $C_6H_2Me(NO_2)_3 \cdot NaO \cdot C_4H_9$, which explodes when

dropped into a tube heated at 170° ; it is apparently accompanied by a small proportion of a di- or tri-alkyloxide (compare Busch and Kögel, A., 1910, i, 472).

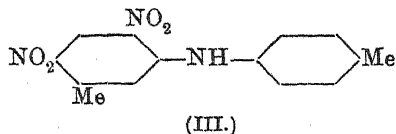
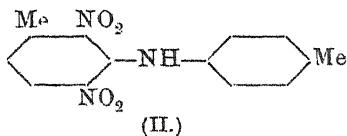
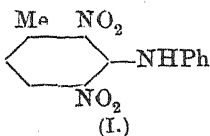
With either alkali hydroxide in presence of an oxidising agent (iodine) or hot alkali hydroxide or carbonate solution, α -trinitrotoluene gives hexanitrodibenzyl. When treated with alkali hydroxide or carbonate, β -trinitrotoluene yields a dinitro-*m*-cresol, m. p. 101° (compare Will, A., 1914, i, 509), and a large proportion of more complex products, whilst the γ -compound gives, in small amounts, a dinitro-*m*-cresol, m. p. $72-73^{\circ}$ (Will, *loc. cit.*), and a crystalline compound insoluble in alkali, possibly a dibenzyl or stilbene derivative. In all cases, dark, amorphous, explosive substances were isolated from the products of the action of alkalis.

α -Trinitrotoluene yields brown, complex compounds under the prolonged action of aqueous ammonia. With alcoholic ammonia, the β -compound reacts readily in the cold, giving β -dinitrotoluidine, m. p. $95-96^{\circ}$ (compare Hepp, A., 1883, 315); with aqueous ammonia, the β -compound yields a small proportion of β -dinitrotoluidine, and the γ -compound γ -dinitrotoluidine, m. p. $190-192^{\circ}$.

α -Trinitrotoluene forms an additive compound with *p*-toluidine (compare Jackson and Clarke, P., 1906, 83). With aniline, β -trinitrotoluene yields a phenyldinitrotolylamine, m. p. $114-115^{\circ}$, of the probable constitution (I) (compare Hepp, *loc. cit.*), and with *p*-toluidine, a dinitroditylamine, probably (II), which forms red, prismatic crystals, m. p. 131° .

p-toluidine, γ -trinitrotoluene gives an additive compound, $C_{14}H_{14}O_6N_4$, which crystallises in yellow needles, becomes orange-red at 147° , m. p. 154° ; in hot alcoholic solution, the reaction yields a dinitroditylamine, probably (III), which forms orange, monoclinic plates, m. p. 154° .

With aldehydes in presence of piperidine, α -trinitrotoluene condenses, giving (1) with benzaldehyde, 2 : 4 : 6-trinitrostilbene; (2) with anisaldehyde, 2 : 4 : 6-trinitro-4'-methoxystilbene (compare Pfeiffer and Monath, A., 1906, i, 413; 1916, i, 24), and (3) with piperonaldehyde, 2 : 4 : 6-trinitro-3' : 4'-methylenedioxy stilbene, $C_{15}H_9O_8N_3$, which crystallises from benzene in dull yellow prisms, turning scarlet on keeping or on being heated, owing to loss of benzene of crystallisation; m. p. (solvent-free), $156-157^{\circ}$. This reaction is not shown by either the β - or the γ -compound, even at 130° , only a brown, amorphous substance being obtained.



With phenanthrene, all three trinitrotoluenes form additive compounds, $C_{21}H_{15}O_6N_3$: (1) α -compound, bright yellow needles, m. p. 98—99°; (2) β -compound, pale yellow, prismatic plates, m. p. 105°; (3) γ -compound, dull yellow, acicular prisms, m. p. 83°.

The four substances examined react differently with alkalis, but in all cases reduction occurs, this probably proceeding to the formation of an amine, the amino-group of which is then replaced by hydroxyl with liberation of ammonia. Complex phenolic compounds are also apparently formed in considerable proportions. In the case of α -trinitrotoluene, this reduction is accompanied by an oxidation process, yielding hexanitrodibenzyl; non-phenolic compounds obtained from *s*-trinitrobenzene and γ -trinitrotoluene may also result from oxidation.

A sample of crude γ -trinitrotoluene was found to contain a dark, amorphous substance, which explodes when heated. T. H. P.

α - and β -Aminoalkyl(aryl)benzenes and their Derivatives.
A. OGATA (*J. Pharm. Soc. Japan*, 1919, **445**, 193—216).—For the study of the relation between the chemical constitution of amino-compounds and their local narcotic action, the author has prepared (1) five β -aminoalkyl(aryl)benzenes; (2) five α -aminoalkyl(aryl)benzenes; (3) four aryl derivatives of (1) and (2); (4) two *N*-alkylaryl derivatives of (1); and (5) three mixed secondary alkylamines. Primary amines can be prepared from nitriles by reduction with sodium. The author obtained β -phenylethylamine from phenylacetone nitrile in 68% yield, and isohexylamine from isohexonitrile. β -Phenylisopropylamine, $CH_2Ph \cdot CHMe \cdot NH_2$, can easily be prepared by the action of ammonium formate (2 grams) on benzyl methyl ketone (2 grams) at 180.—200°. Similarly were prepared β -aminoisohexylbenzene [β -amino- α -phenyl- δ -methylpentane], $CH_2Ph \cdot CH(NH_2) \cdot CH_2Pr^\beta$, b. p. 121°/8 mm. (hydrochloride, $C_{12}H_{19}N \cdot HCl$, m. p. 230—231°), β -amino-octylbenzene [β -amino- α -phenyloctane], $CH_2Ph \cdot CH(NH_2) \cdot [CH_2]_5 \cdot CH_3$, b. p. 145°/75 mm. (hydrochloride, m. p. 134—136°), $\alpha\beta$ -diphenylethylamine, α -phenylethylamine in 65% yield, α -aminoisohexylbenzene [α -amino- α -phenyl- δ -methylpentane], $NH_2 \cdot CHPh \cdot CH_2 \cdot CH_2Pr^\beta$, b. p. 146°/3 mm. (hydrochloride, m. p. 289°), and α -aminoheptylbenzene [α -amino- α -phenylheptane], $NH_2 \cdot CHPh \cdot [CH_2]_5 \cdot CH_3$, b. p. 145°/15 mm. (hydrochloride, m. p. 185—186°), from benzyl isobutyl ketone, benzyl *n*-hexyl ketone, deoxybenzoin, phenyl isoamyl ketone, and phenyl *n*-hexyl ketone respectively.

Secondary amines, such as di- β -phenylethylamine, benzyl- β -phenylisopropylamine, $CH_2Ph \cdot NH \cdot CHMe \cdot CH_2Ph$, b. p. 194°/24 mm. (hydrochloride, m. p. 186·5°), and benzyl- β -phenylethylamine have been obtained by reducing with sodium the condensation products of β -phenylethylamine and phenylacetaldehyde, of β -phenylisopropylamine and benzaldehyde, and of β -phenylethylamine and benzaldehyde respectively. isoAmylisoheptylamine, $CH_2Pr^\beta \cdot CH_2 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2Pr^\beta$, b. p. 208°/758 mm. (hydrochloride, m. p. 258—259°; stannichloride, m. p. 198°), was pre-

pared by the condensation of *isoamyl* bromide and *isohexylamine*, and *isoamylheptylamine*, $C_{12}H_{27}N$, b. p. $229^{\circ}/761$ mm. (*hydrochloride*, m. p. 235°), by the condensation of *isoamyl* bromide and *n*-heptylamine.

Tongue-tests proved that the hydrochlorides of β -amino- α -phenyloctane, $\alpha\beta$ -diphenylethylamine, α -phenylethylamine, benzyl- β -phenylisopropylamine, and *isoamylisohexylamine* have hypnotic action.

CHEMICAL ABSTRACTS.

Preparation of Explosives. THOMAS CAMPBELL JAMES, JAMES IVOR MORGAN JONES, and ROBERT ILLTYD LEWIS (Eng. Pat., 130357).—Trinitrophenylmethylnitroamine (tetryl) forms stable condensation products with aromatic amines, and these can be readily nitrated with warm nitric acid, forming nitro-compounds suitable for use as high explosives. In the case of trinitrophenylmethylnitroamine and aniline, picrylaniline, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_5$, is obtained, and this, when nitrated, yields hexanitrodiphenylamine.

C. A. M.

Action of Bromine on some Derivatives of Diphenylamine. HUGH RYAN and WILLIAM O'RIORDAN (*Proc. Roy. Irish Acad.*, 1919, **34**, 218—225).—The method given by Berger (compare Buisson, "Le Problème des Poudres") for the estimation of the total amount of diphenylamine, either free or as nitroso-derivative, present as stabiliser in a powder, depends on the conversion of the base into its tetrabromo-compound. By boiling the powder with dilute sodium hydroxide solution, the diphenylnitrosoamine is converted into diphenylamine; the distillate is then treated with excess of bromine, and the amount not used in the formation of the tetrabromodiphenylamine estimated volumetrically.

The authors' experiments show that the prolonged action of bromine on diphenylnitrosoamine in chloroform solution and in presence of sunlight yields mainly hexabromodiphenylamine, m. p. 223° (compare Gnehm, this Journal, 1876, 83), which is also obtained under similar conditions from tetrabromodiphenylamine; the latter represents the first product of the action of bromine on diphenylnitrosoamine.

Since some of the nitro-derivatives of diphenylamine and diphenylnitrosoamine are appreciably volatile in steam, and would hence accompany the diphenylamine in the distillate of Berger's method, the action of bromine on 4-nitro-, 2:10-, and 4:10-dinitrodiphenylnitrosoamines, 2:4-, 2:10-, and 4:10-dinitrodiphenylamines, and 2:4:8:10-tetranitrodiphenylamine has been investigated; of these compounds, the first three and the last have been found among the products of the interaction of diphenylamine with the oxy-acids of nitrogen. With the exception of the tetranitro-compound, all these compounds react with bromine in chloroform solution, the only product being in each case a dibromo-derivative. The derivatives of diphenylnitrosoamine lose the nitroso-group on bromination and yield the same bromo-compounds as the corresponding nitrodiphenylamines.

It is evident that Berger's method (see above), and also that of Dreger (A., 1909, ii, 708), will give untrustworthy results if any of the volatile nitro-compounds formed from diphenylamine in a powder escape interaction with the alkali, or if a mixture of tetra- and hexa-bromodiphenylamines is formed in consequence either of rise of temperature caused by rapid addition of the bromine or of prolonged contact of the bromine with the product.

Dibromo-4-nitrodiphenylamine, $C_{12}H_8O_2N_2Br_2$, forms bright yellow needles, softening at 212° , m. p. 216° . *Dibromo-2:4-dinitrodiphenylamine*, $C_{12}H_7O_4N_3Br_2$, prepared from 2:4-dinitrodiphenylamine, forms orange, rhombic prisms, m. p. 195.5° , and may be identical with the compound, m. p. 196° , obtained by Leymann (A., 1882, 1057). *Dibromo-2:10-dinitrodiphenylamine* forms felted, yellow needles, m. p. $185-186^\circ$. *Dibromo-4:10-dinitrodiphenylamine* forms pale yellow needles, m. p. 247° . T. H. P.

Action of Nitric Acid and Nitrous Acid on Diphenylamine.

I. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1918 **34**, 194—204).—The experiments here described were all carried out at the ordinary temperature and at low concentrations. Under these conditions, prolonged interaction of equivalent amounts of diphenylamine and nitric acid in acetic acid solution forms only the nitrate of the base, whilst when a greater proportion of the acid is taken, one portion of the amine is converted into a brown, resinous solid and another portion into nitro-derivatives of diphenylamine, among which the 2:10-dinitro-, 4:10-dinitro-, and 2:4:8:10-tetranitro-derivatives have been identified; in only one experiment was a trace of 2:10-dinitrodiphenylnitrosoamine obtained.

Under similar conditions, the nitration of diphenylnitrosoamine proceeds quite differently. When two or more equivalents of nitric acid are used per one equivalent of diphenylnitrosoamine, the colour of the solution changes slowly from orange to orange-yellow or yellow, with separation of the sparingly soluble 2:10-dinitrodiphenylnitrosoamine. The latter is not formed when only one equivalent of acid is employed, the products then being 4-nitrodiphenylnitrosoamine, and probably a small amount of 2-nitrodiphenylnitrosoamine. When larger proportions of nitric acid are employed, the acetic acid solution is found to contain 2:4:8:10-tetranitrodiphenylamine and 4:10-dinitrodiphenylamine, together with other polynitro-compounds which have not been isolated pure. Three apparently different dinitrodiphenylamines have been prepared; all of these are pale yellow and melt with decomposition, binary mixtures melting several degrees lower than either of the constituents. The fact that these three compounds lose nitric oxide when heated may have a bearing on the heat tests for nitrocellulose powders stabilised by addition of diphenylamine.

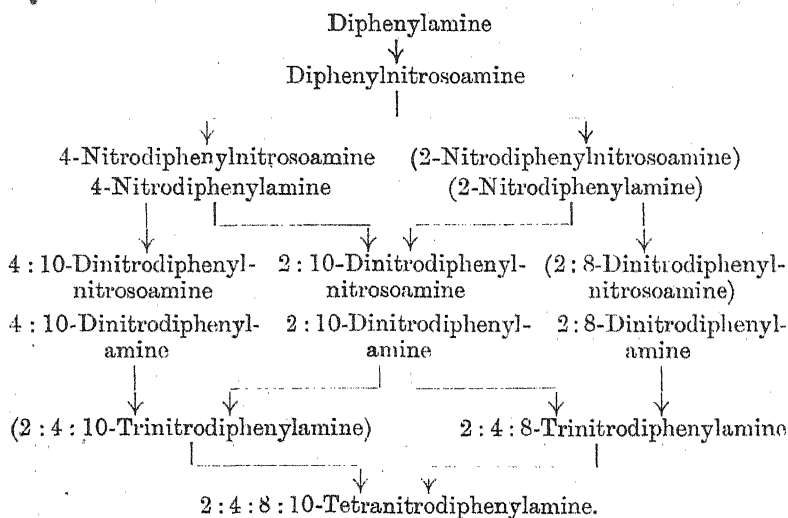
The action of nitric acid on diphenylamine in presence of nitrous acid has also been investigated. In this case, the main product is always a dinitrodiphenylnitrosoamine, the formation of which is

regarded as an indication of the completion of the stabilising action of the diphenylamine.

4:10-Dinitrodiphenylnitrosoamine (?), $C_{12}H_8O_5N_4$, obtained by the action in the cold of nitric acid of D 1.43 (6 mols.) on 4-nitrodiphenylnitrosoamine (1 mol.) in glacial acetic acid solution, is a yellowish-white solid, m. p. 155—159° (decomp.) T. H. P.

Action of Nitric Acid and Nitrous Acid on Diphenylamine.

II. HUGH RYAN and PHYLLIS RYAN (*Proc. Roy. Irish Acad.*, 1919, **34**, 212—217. Compare preceding abstract).—Owing to the ease with which the nitroso-group may be split off from nitrodiphenylnitrosoamines, the action of nitric acid on diphenylamine and diphenylnitrosoamine has been examined in the inert solvent, carbon tetrachloride. In this case, the reactions were complicated by separation of the solution into two layers with different relative concentrations of the reacting compounds, but in general the nitrations follow courses similar to those exhibited in acetic acid. Combination of the two sets of results gives the following scheme for the course of the reaction between nitric acid, nitrous acid, and diphenylamine at the ordinary temperature, and at low concentrations of the interacting compounds:



The compounds shown in brackets have not been isolated, but are probably present in some of the fractions obtained. T. H. P.

Melting Point of Pure Phenol. HENRI LEROUX (*J. Pharm. Chim.*, 1919, [vii], **20**, 88—91).—Pure phenol melts at 40.85° and boils at 182°/760 mm. Phenol is hygroscopic, and the presence of 0.2% of water lowers the melting point to 40°. W. P. S.

Process for the Preparation of Primary Alcohols. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat., 122630).—Ethylene oxide readily lends itself to the practical synthesis of primary alcohols provided that it is caused to react on an ethereal solution of an aromatic Grignard reagent in the gaseous form at temperatures between 0° and 10° instead of in ethereal solution at -15° , as hitherto employed. Under these conditions, almost theoretical yields are obtained. Examples are given of the synthesis of phenylethyl alcohol, *p*-tolylethyl alcohol, *p*-methoxyphenylethyl alcohol, and 6-methoxy-*m*-tolylethyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] G. F. M.

Synthesis of certain Substituted Pyrogallol Ethers, including a New Acetophenetidide derived from the Ethyl Ether of Syringic Acid. MARSTON TAYLOR BOGERT and JACOB EHRLICH (*J. Amer. Chem. Soc.*, 1919, **41**, 798—810).—By conversion of the ethyl ether of syringic acid into the corresponding chloride and amide, and subjection of the latter to the Hofmann reaction, the authors have obtained 3:5-dimethoxyphenetidine, which on acetylation yields 3:5-dimethoxyacetophenetidide; this compound exhibits marked antipyretic properties, and is not more toxic than phenacetin. Syringic acid was obtained in 75% yield from 3:4:5-trimethoxybenzoic acid by a modification of Bogert and Isham's method (*A.*, 1914, **i**, 532).

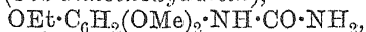
3:5-Dimethoxy-4-ethoxybenzoic acid (syringic acid ethyl ether), $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CO}_2\text{H}$, forms lustrous, white, sword-shaped needles, m. p. $123\text{--}124^{\circ}$ (corr.), and remains apparently unchanged at 300° . Its methyl ester, $\text{C}_{12}\text{H}_{10}\text{O}_5$, colourless, rhombic plates or long needles, m. p. $64\cdot5\text{--}65^{\circ}$ (corr.), ethyl ester, hexagonal crystals, m. p. $46\text{--}47^{\circ}$ (corr.), b. p. $195\text{--}196^{\circ}/30\text{ mm.}$, and amide, $\text{C}_{10}\text{H}_{13}\text{O}_3\cdot\text{CO}\cdot\text{NH}_2$, white, glistening leaves, m. p. $154\text{--}155^{\circ}$ (corr.), were prepared.

3:5-Dimethoxy-*p*-phenetidine (3:5-dimethoxy-4-ethoxyaniline), $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NH}_2$, forms pale brown needles, m. p. $92\text{--}93^{\circ}$ (corr.), and in the air undergoes gradual oxidation to a blue, amorphous substance. In aqueous solution, the amine gives a deep emerald coloration with ferric chloride and spangles of silver with silver nitrate. In concentrated sulphuric acid, it gives a colourless solution, but addition of the solid amine to concentrated nitric acid produces a deep crimson coloration, changing to clear yellow. When diazotised and coupled with α -(β -naphthol in alkaline solution, the amine yields a deep crimson (bright vermilion) dye.

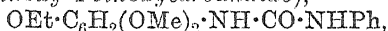
3:5-Dimethoxyaceto-*p*-phenetidide (3:5-dimethoxy-4-ethoxyacetanilide), $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{NHAc}$, forms long, white needles, m. p. 129° (corr.), and also crystallises with $1\text{H}_2\text{O}$ in white prisms, m. p. 90° (corr.); it is not volatile in a current of steam. 2-Bromo-3:5-dimethoxy-4-ethoxyacetanilide, $\text{C}_{12}\text{H}_9\text{O}_4\text{NBr}$, was obtained crystalline.

3:5-Dimethoxy-4-ethoxyphenol, $\text{OEt}\cdot\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{OH}$, to which the name *homoantiarol* (compare Kiliani, *A.*, 1897, **i**, 91; Graebe

and Suter, A., 1905, i, 703) is given, forms long, hair-like, pale yellow needles, m. p. 119° (corr.), and volatilises slowly even at 100° ; it responds to the ordinary reagents for free hydroxyl groups. 1-Iodo-3:5-dimethoxy-4-ethoxybenzene, $\text{OEt}\cdot\text{C}_6\text{H}_2\text{I}(\text{OMe})_2$, crystallises in yellow needles, m. p. 53° (corr.), and exhibits a powerful odour resembling that of iodoform. 3:5-Dimethoxy-4-ethoxyphenylcarbamide (3:5-dimethoxydulcin),



forms white needles, m. p. 182° (corr.), and, unlike dulcin, is practically tasteless. 3:5-Dimethoxy-4-ethoxy-s-diphenylcarbamide (3:5-dimethoxy-4-ethoxycarbanilide),



forms long, white, hair-like needles, m. p. 185° (corr.). 3:5-Dimethoxy-4-ethoxybenzeneazo- β -naphthol (3:5-dimethoxyphenetidineazo- β -naphthol), $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, forms dark red plates with a bronze-like lustre, m. p. 130° (corr.), and dyes silk and cotton salmon-pink and wool bright orange, the colours being fast against water, soap, dilute acid, and light. T. H. P.

Chemical Constituents of Bulbus Scillae. ERNST BUSCHMANN (*Arch. Pharm.*, 1919, 257, 79—86).—For purposes of investigation, it is essential to use fresh material, since the dried substance contains so much syrupy matter that the extraction of the active principles is practically impossible.

The coarsely powdered material was repeatedly extracted with cold water, and the extracts were treated successively with lead acetate, sodium phosphate, and ethyl acetate; the last removed a small quantity of yellow, crystalline material, the amount of which was too small for further investigation. The presence of choline in the residual aqueous solution was ascertained by the isolation of its platinichloride, m. p. 241° , and aurichloride, m. p. 261° . The residue left from the treatment with water was extracted with alcohol, and the extract was treated successively with light petroleum (b. p. not above 50°), ether, and chloroform. In this manner, there were obtained (i) xanthoscillide, lemon-yellow needles, m. p. 117 — 118° , which in an impure form constitutes Merck's scillin, scillisterol, m. p. 163 — 164° [acetate, m. p. 133 — 134° ; bromoacetate, m. p. 196° (decomp.)], phytosterol, m. p. 134° (acetate, m. p. 125 — 126°), and a brown oil (D 0.9248, iodine number 57.74—60.03, Köttstorfer number 192.65—199.22) in which the presence of formic and palmitic acids, probably also of acetic or propionic acid and oleic acid, was established; (ii) a phytosterol-glucoside, colourless, slender, indistinct needles, m. p. 290° (decomp.); and (iii) a small amount of long, slender needles which could not be further investigated.

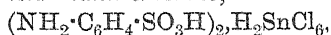
The aqueous extract which had been treated with lead acetate gradually deposited a brownish-yellow precipitate, from which a strong organic acid was isolated, the investigation of which is not complete; a brown dye was also present. H. W.

Some Esters of *p*-Nitro- and *p*-Amino-benzoic Acid. S. V. HINTIKKA and LINDA MELANDER (*Ann. Acad. Sci. Fennicae*, 1919, [A], 10, No. 13; from *Chem. Zentr.*, 1919, i, 836—837).—*Bornyl p-nitrobenzoate*, m. p. 134°, is prepared by heating a mixture of borneol and *p*-nitrobenzoyl chloride. *Camphenyl p-nitrobenzoate*, needles, m. p. 98°, is similarly obtained from camphenilol (m. p. 68—69°, $[\alpha]_D +19.12^\circ$). *Fenchyl p-nitrobenzoate* crystallises in needles, m. p. 108—109° (the fenchyl alcohol was prepared from fenchone and had $[\alpha]_D -8.43^\circ$). *Bornyl p-aminobenzoate*, prepared by reducing the corresponding nitro-ester with stannous chloride and hydrochloric acid, forms needles or large, regular crystals, m. p. 144°, whilst its *acetyl* derivative crystallises in plates, m. p. 158°. Reduction of camphenyl *p*-nitrobenzoate leads to a mixture of the *amino*-ester, plates, m. p. 165°, and a substance, m. p. 126—129°. Attempts to reduce fenchyl *p*-nitrobenzoate by tin or stannous chloride and hydrochloric acid, or by zinc and acetic acid, led to resinous products. The action of hydrogen in the presence of colloidal palladium on an alcoholic solution of the fenchyl ester yielded a product, analyses of which gave results approximating to those required by the formula $C_{17}H_{23}O_2N$; it was an amino-compound, which, however, could not be purified. The ester could not be prepared from a mixture of *p*-aminobenzoic acid, fenchyl alcohol, and concentrated sulphuric acid, which yielded an oil, b. p. 166—168°/10 mm., $D_4^{25} 0.9535$, $n_D^{25} 1.5193$, the formation of which was due to the action of sulphuric acid on the alcohol; it is probably an unsaturated hydrocarbon of high molecular weight.

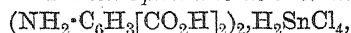
H. W.

Preparation of Organic Stanno- and Stanni-chlorides.
III. Compounds of the Amino-acids. J. G. F. DRUCE (*Chem. News*, 1919, 119, 73—74. Compare *ibid.*, 1919, 118, 1, 87).—The following organic derivatives of stannous and stannic chlorides have been prepared and characterised. *Anthranilic acid stannochloride*, $CO_2H \cdot C_6H_4 \cdot NH_2 \cdot H_2SnCl_3$, is prepared by warming 1.7 grams of *o*-nitrobenzoic acid with 3.6 grams of granulated tin and 30 c.c. of hydrochloric acid diluted with an equal volume of water. On cooling, after the solution of the tin, the salt separates in colourless, microcrystalline needles, which are washed with diluted hydrochloric acid and dried in the air. The salt softens at 85° and melts at 125° to a colourless liquid. A solution in hydrochloric acid gives a white precipitate with mercuric chloride and a brownish-black precipitate with hydrogen sulphide. This compound has also been prepared by crystallising the component salts together. *Anthranilic acid stannichloride*, $(NH_2 \cdot C_6H_4 \cdot CO_2H)_2 \cdot H_2SnCl_6$, is prepared by dissolving 3 grams of the first-mentioned compound in diluted hydrochloric acid and passing a slow stream of chlorine through the solution for three hours. On concentrating, deliquescent needles separate from the solution. This salt was also prepared by crystallising a mixture of the component salts. *m-Aminobenzoic acid stannochloride*, $(NH_2 \cdot C_6H_4 \cdot CO_2H)_2 \cdot H_2SnCl_4$, is prepared by an

analogous method to the first-named salt. It crystallises in a mass of feathery needles, m. p. 240° ; it is not very soluble in water, but the solution is strongly acid, and boiling does not cause hydrolysis. *m-Aminobenzoic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, is prepared similarly to the corresponding ortho-compound. It forms short, radiating masses of colourless crystals, m. p. 193° . *p-Aminobenzoic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, may be prepared by crystallising a mixture of the component salts or by reducing *p*-nitrobenzoic acid with tin and hydrochloric acid. Attempts to prepare the corresponding stannochloride yielded only the stannichloride. This compound crystallises in small, pale yellow, brittle needles, and does not melt at temperatures up to 315° . *Sulphanilic acid stannichloride*,



is prepared by crystallising a solution of the component salts from hot diluted hydrochloric acid. It forms a white, microcrystalline powder which is sparingly soluble in cold water. With warm water, metastannic acid separates; the salt does not melt, but darkens and decomposes at 270° . *4-Aminophthalic acid stannochloride*,



is prepared by reducing 4-nitrophthalic acid with tin and hydrochloric acid. It forms short, white needles, m. p. 274° ; it is soluble in cold water, but hydrolysed on heating. *4-Aminophthalic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{CO}_2\text{H}]_2)_2 \cdot \text{H}_2\text{SnCl}_6$, is obtained by warming 2 grams of 4-nitrophthalic acid and 6.9 grams of stannous chloride with 100 c.c. of diluted hydrochloric acid for two hours. It forms small, pale yellow crystals, m. p. 182° . *Aminosalicilic acid stannichloride*, $(\text{NH}_2 \cdot \text{C}_6\text{H}_3[\text{OH}] \cdot \text{CO}_2\text{H})_2 \cdot \text{H}_2\text{SnCl}_6$, is prepared by reducing nitrosalicilic acid with stannous chloride in alcoholic hydrochloric acid; it forms small, brown, prismatic crystals, m. p. 128° . It is soluble in water, but is hydrolysed on warming.

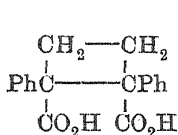
J. F. S.

Heterocinnamic Acids of Erlenmeyer, jun. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1048—1054).—The author has repeated the experiments of Erlenmeyer by which the heterocinnamic acids were stated to be formed, and is unable to obtain these substances. It would therefore appear that these compounds are not pure substances and cannot be obtained from pure cinnamic acid.

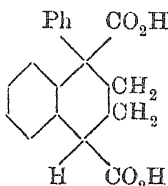
J. F. S.

Constitution of the isoAtropic Acids. L. SMITH (*Lunds Univ. Årsskr.*, 1919, [ii], **14**, 3—16; from *Chem. Zentr.*, 1919, i, 834—836).—Anhydrous atrolactic acid is smoothly transformed into α -isoatropic acid when heated at 140 — 160° in an atmosphere of carbon dioxide; at 200° , a mixture of the α - and β -acids, containing about 33% of the latter, is formed. Concentrated alkalis convert the α -acid into the β -acid. It is therefore possible that the

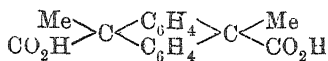
acids are *cis-trans*-isomerides, which is consistent with the formulæ previously proposed for them:



(I.)



(II.)



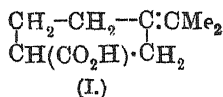
(III.)

The choice between these formulæ is rendered possible by the fact that the first contains two similarly situated asymmetric carbon atoms; the second has two dissimilar atoms, whilst the third does not possess an asymmetric carbon atom. Since α - and β -isoatropic acids can be resolved by phenylethylamine, formulæ I and III are excluded. If the acids are really *cis-trans*-isomerides, it should be possible to obtain the active *trans*-form from the active *cis*-form, and this can actually be effected by the action of sodium ethoxide on the *d*- α -acid, whereby the *d*- β -acid is produced. The action of alcoholic hydrogen chloride on the α -acid leads to the formation of a hydrogen ester which, when hydrolysed, yields a mixture of α - and β -isoatropic acids. The conversion, however, does not occur during esterification, as Liebermann assumed, but during hydrolysis. The hydrogen ester of the α -acid is an α -compound which, when hydrolysed in the cold, yields α -acid mixed with only 10% of the β -isomeride. The hydrogen ester of the β -acid belongs to the β -series, and, contrary to Liebermann's data, cannot be converted by heat or by crystallisation from acetic acid into the α -isomeride. β -isoAtropic acid and its hydrogen ester yield only β -acid and decomposition products when treated with acetic acid and concentrated hydrochloric acid. Attempts to effect the interconversion by means of ultra-violet light were unsuccessful.

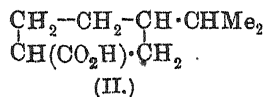
α -isoAtropic acid, m. p. 238.5—239° (corr.), or rather lower when heating is effected too slowly, is best prepared by heating anhydrous atrolactic acid in an atmosphere of carbon dioxide during thirty hours at 140—160°. It is converted by boiling alcoholic sodium ethoxide or aqueous barium hydroxide solution into β -isoatropic acid, m. p. 208.5—209° (corr.). The latter can be resolved into its components with the aid of *l*-phenylethylamine in aqueous-alcoholic solution, when the salt of the *d*-acid separates. *d*- β -isoAtropic acid has m. p. 196.5—197.5° (corr.), $[\alpha]_D + 8.95^\circ$ in alcoholic solution. *l*- β -isoAtropic acid, m. p. 196.5—197°, $[\alpha]_D - 8.8^\circ$ in alcohol, is similarly obtained by the help of *d*-phenylethylamine. *d*- α -isoAtropic acid, prepared by resolving the *r*-acid with *d*-phenylethylamine, has $[\alpha]_D + 7.25^\circ$ in alcoholic solution, m. p. 239° after darkening, and softening at 234° when not too slowly heated. *l*- α -isoAtropic acid is isolated from the residues left

from the separation of the *d*-isomeride or by treatment of the lævorotatory mixture of acids which is then produced with *l*-phenylethylamine; it has $[\alpha]_D -7.26^\circ$ in ethyl-alcoholic solution. *Ethyl hydrogen β -isoatropate* crystallises in plates, m. p. 116° (corr.). *Ethyl hydrogen α -isoatropate* has m. p. 186° . H. W.

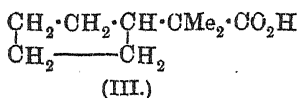
Camphenecamphoric Acid. S. V. HINTIKKA (*Ann. Acad. Sci. Fennicae*, 1919, [A], 6, iii; from *Chem. Zentr.*, 1919, i, 839—840). —It has been shown previously (A., 1914, i, 409) that carbocamphenilone is formed by the dry distillation of lead hydroxycamphenilinate, and is converted by hydrogen peroxide into camphenecamphoric acid, $\begin{array}{c} \text{CH}_2-\text{CH}_2-\text{CH}\cdot\text{CMe}_2\cdot\text{CO}_2\text{H} \\ | \\ \text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2 \end{array}$ (A., 1914, i, 973). Doubt has been cast on the validity of this formula by Aschan (A., 1914, i, 692), but it may be regarded as established by Lipp's synthesis of the acid (A., 1914, i, 542) and by the complete synthesis of camphenilone (A., 1914, i, 852). The results of further investigations are most readily explained with the help of Lipp's formula. The constitution of carbocamphenilone (annexed formula) follows from its reconversion by sodium hydroxide into hydroxycamphenilanic acid. When camphenecamphoric acid is distilled under ordinary pressure (Aschan, A., 1911, i, 797), it yields a liquid, unsaturated acid, $\text{C}_9\text{H}_{14}\text{O}_2$, and an acid, $\text{C}_{10}\text{H}_{14}\text{O}_3$, m. p. 134° ; the former probably has the structure (I), since, when reduced with hydrogen in the presence of palladium, it gives an acid, $\text{C}_9\text{H}_{16}\text{O}_2$, which appears to be identical with dihydrocamphoceanic acid (II) (Bouveault and Blanc, A., 1908, i, 134; 1909, i, 108; Hintikka, A., 1914, i, 838).



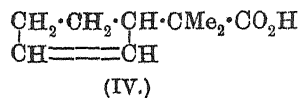
(I.)



(II.)



(III.)



(IV.)

For purposes of comparison, *cyclopentaneisobutyric acid* (III) has been prepared, since the formation of the corresponding unsaturated acid (IV) by the decomposition of camphenecamphoric acid is a possibility. The ketonic nature of the acid, $\text{C}_{10}\text{H}_{14}\text{O}_3$, is confirmed by the isolation of a phenylhydrazone; since the acid is converted by cautious heating with potassium hydroxide solution or by boiling with alcoholic sodium methoxide or ethoxide into camphenecamphoric acid, it may be regarded as camphenilone- α -carboxylic

acid (annexed formula). It is probably identical with the acid obtained by Houben and Willfroth (A., 1913, CH₂:CH—CMe₂, i, 970). The dry distillation of a number of salts of camphenecamphoric acid has been further investigated. The lead salt yields camphenilone, which is also obtained to some extent from the uranyl and ferric salts, but not from the calcium or copper salt.

The following data are recorded. Hydroxycamphenilanic acid has m. p. 176—177°, is optically inactive, and gives camphenilone with lead peroxide and sulphuric acid. The acid, C₉H₁₆O₂, prepared by reduction of the acid, C₉H₁₄O₂, has b. p. 138—139°/10 mm., and is stable towards permanganate; the corresponding amide forms leaflets, m. p. 169°. cycloPentaneisobutyric acid is a readily volatile oil prepared by the catalytic reduction and subsequent hydrolysis of ethyl cyclopenteneisobutyrate; the corresponding amide has m. p. 141—142°, whilst cyclopenteneisobutyramide melts at 136—137°. The phenylhydrazone of camphenilone- α -carboxylic acid, C₁₆H₂₀O₂N₂, has m. p. 142—143°. H. W.

Oxidation of Benzaldoxime. J. BOUGAULT and P. ROBIN (*Compt. rend.*, 1919, 169, 341—343).—The oximes of the aldehydes which would apparently be formed by the elimination of carbon dioxide from α -ketonic acids during oxidation with iodine and sodium carbonate do not give on similar treatment the same products of oxidation as the oximes of the α -ketonic acids themselves. Thus, whilst the oxime of phenylglyoxylic acid gives benzonitrile and diphenylglyoxime peroxide, neither of these substances could be detected among the oxidation products of benzaldoxime. The oxime was treated in benzene solution with aqueous sodium carbonate and iodine. A precipitate of benzaldoxime peroxide, CHPh:N·O·O·N:CHPh, was formed, and from the benzene layer benzoylbenzaldoxime, CHPh:N·OBz, and dibenzenyloxozoxime, CPh<math display="block">\begin{array}{c} \text{NO} \\ \diagup \quad \diagdown \\ \text{CPh} \quad \text{CPh} \end{array}>CPh, were isolated and identified. The latter two substances were separated by forming the easily decomposed iodine additive product of dibenzenyloxozoxime, which is almost insoluble in ether. G. F. M.

Pungency of Synthetic Aromatic Ketones Related to Zingerone. LEONORE KLETZ PEARSON (*Pharm. J.*, 1919, 103, 78—80).—The substances are of the type CHPh:CH·CO·R and CH₂Ph·CH₂·CO·R, where one or more hydrogen atoms of the benzene nucleus is replaced by one or more hydroxy- or methoxy-groups, and where R represents the methyl, ethyl, or phenyl radicle. Similar compounds have been studied from the same point of view by Nomura and Nozawa (A., 1918, i, 438); the authors have, however, been able to make several additional generalisations.

The primary, unsaturated condensation products alone, with the exception of *o*-hydroxystyryl methyl ketone, develop no appreciable

pungency on long contact with the tongue; in alcoholic solution, the pungency appears, as a rule, slowly. In the case of the corresponding saturated compounds, the pungency develops quickly, both alone and in alcoholic solution. β -3:4-Methylenedioxyphenylethyl methyl ketone is an exception in that it develops no appreciable pungency by itself. In every case, the unsaturated ketone was much more pungent than the corresponding saturated compound. The replacement of the hydrogen of the phenolic hydroxy-group of zingerone by an acyl radicle appears to have very little effect on the pungency of the compound. On the other hand, 3:4-methylenedioxystryl methyl ketone and 3:4-methylenedioxyphenylethyl methyl ketone, though containing no free hydroxy-groups, are much more pungent than the corresponding 4-hydroxy-3-methoxy-derivatives, to which they are closely related.

The replacement of the *meta*-hydrogen of the benzene nucleus in *p*-hydroxyphenylethyl methyl ketone by a methoxy-group brings about a decided increase in pungency. The substitution of a bromine atom in this position appears to have a similar effect.

An increase in the weight of the side-chain causes a decided increase in the pungency of the compound. The exceptional pungency of *o*-hydroxystryl methyl ketone is an outstanding feature of the experiments.

The experimental method of testing the substances consisted in dissolving the compound (0.1 gram) in alcohol (10 c.c.), diluting 1 c.c. of this solution to 3 c.c. or 10 c.c. with water or alcohol (or a mixture), and continuing the dilution in this way until the pungency was found to have become imperceptible. In the case of the more concentrated alcoholic solutions, one or two drops were placed on the tongue; the effect of the alcohol rapidly disappeared, and the pungency became perceptible. With more dilute aqueous solutions, a quantity was taken into the mouth and allowed to remain there for about three seconds.

4-Hydroxy-3-methoxystryl ethyl ketone, prepared from vanillin and methyl ethyl ketone, is an almost colourless, crystalline solid, m. p. 94°. *3:4-Dihydroxystryl methyl ketone* forms pale brown cubes, m. p. 176°. H. W.

Halogenation of Juglone: New Type of Naphthalene Dyes.

A. S. WHEELER and J. W. SCOTT (*J. Amer. Chem. Soc.*, 1919, **41**, 833—841).—Treatment of juglone (5-hydroxy-1:4-naphthaquinone) in acetic acid solution in the cold with chlorine or bromine yields juglone dichloride or dibromide, which loses one molecule of hydrogen haloid under the action of alcohol, giving 2-chloro-(or bromo-)juglone [2-chloro-(or bromo-)5-hydroxy-1:4-naphthaquinone]. In hot acetic acid solution, the action of chlorine on juglone forms 2:3-dichloro-5-hydroxy-1:4-naphthaquinone, whereas that of bromine under similar conditions yields 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone; both these compounds form acetyl derivatives, and treatment of the tribromo-derivative with alcoholic hydrochloric acid gives 8-chloro-2:3-dibromo-1:4-naphthaquinone.

Further, the 8-bromine atom of the tribromo-compound is replaced by hydroxyl by the action of alcoholic sodium hydroxide, 2:3-dibromo-5:8-dihydroxy-1:4-naphthaquinone resulting.

The tribromojuglone is a brilliant red compound, and constitutes a naphthalene dye of a new type. Its sodium salt, readily prepared by shaking its ethereal solution with aqueous sodium carbonate, is an indigo-blue compound, and dyes silk a fine champagne colour and wool a tan colour, which may be modified by the use of mordants; in both cases, the colour is fast against washing and ironing, and fades only after long exposure to a southern light. Cotton requires a mordant, and, when tannin is used in this capacity, assumes an éceru colour. According to its constitution, juglone itself should act as a dye, but attempts to prepare its sodium salt result in its oxidation, whilst careful halogenation of juglone in the cold yields an unstable additive product.

5-Hydroxy-1:4-naphthaquinone 2:3-dichloride (juglone dichloride), $C_{10}H_6O_3Cl_2$, forms lemon-yellow plates, turning brown at 150° , m. p. $159-160^\circ$.

2-Chloro-5-hydroxy-1:4-naphthaquinone (2-chlorojuglone), $C_{10}H_5O_3Cl$, forms small, flat, yellowish-brown needles, and emits violet vapour at above 130° , m. p. 166° . Its *acetyl* derivative, $C_{12}H_7O_4Cl$, crystallises in transparent, brownish-yellow plates, m. p. 147° .

2:3-Dichloro-5-hydroxy-1:4-naphthaquinone (2:3-dichlorojuglone), $C_{10}H_4O_3Cl_2$, forms lustrous, golden-brown needles, m. p. 149° (dark red liquid); its *acetyl* derivative, $C_{10}H_3O_2Cl_2 \cdot OAc$, forms yellow plates, m. p. 154° (dark brown liquid).

5-Hydroxy-1:4-naphthaquinone 2:3-dibromide (juglone dibromide), $C_{10}H_6O_3Br_2$, forms rosettes and fan-shaped groups of yellow, pointed prisms, m. p. 109° .

2-Bromo-5-hydroxy-1:4-naphthaquinone (2-bromojuglone), $C_{10}H_5O_3Br$, forms clusters of translucent, yellowish-brown plates, m. p. 166° (almost black liquid). Its *acetyl* derivative, $C_{10}H_4O_2Br \cdot OAc$, forms golden-brown plates, m. p. 148° (dark yellow liquid).

2:3:8-Tribromo-5-hydroxy-1:4-naphthaquinone (2:3:8-tribromojuglone), $C_{10}H_3O_3Br_3$, forms brilliant, deep red needles, m. p. 170° , and dissolves in concentrated nitric or sulphuric acid with a red coloration, and in hot sodium carbonate solution, yielding a purple liquid quickly changing to red. Its *sodium* derivative,

$C_{10}H_2O_3Br_3Na$, dissolves readily in water or alcohol, and its *acetyl* derivative, $C_{10}H_2O_2Br_3 \cdot OAc$, crystallises in silky, yellow needles, m. p. 186° . Attempts to methylate tribromojuglone were unsuccessful, and oxidation by means of nitric acid or alkaline permanganate solution gave no definite product.

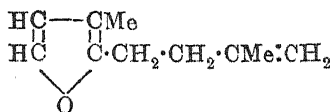
8-Chloro-2:3-dibromo-5-hydroxy-1:4-naphthaquinone (8-chloro-2:3-dibromojuglone), $C_{10}H_3O_3ClBr_2$, forms golden-bronze plates, m. p. 152° (dark red liquid).

2:3-Dibromo-5:8-dihydroxy-1:4-naphthaquinone (2:3-dibromo-

8-hydroxyjuglone), $C_{10}H_4O_4Br_2$, forms small, golden-brown, prismatic needles, and emits vapour at about 160° , m. p. 236° (black liquid). T. H. P.

Solubility of Camphor in Water. H. LEO and E. RIMBACH (*Biochem. Zeitsch.*, 1919, **95**, 306—312).—The solubility of camphor in water at the ordinary temperature is 1 in 598. In Ringer's solution under the same conditions, it is 1 in 577. The solubility falls with rise in temperature. The dissolution of camphor in water is an exothermic process. J. C. D.

Essential Oil of Perilla citriodora, Makino. HEISABURO KONDO and SEITARO YAMAGUCHI (*J. Pharm. Soc. Japan*, 1919, **446**, 263—275).—*Perilla citriodora*, Makino, which belongs to the *Labiatae* group, is known to contain an essential oil in an amount 2—3% of the weight of the dry leaf, having D 0.911—0.913; 59.26% of the oil is citral. The authors have investigated the chemical nature of the remaining portion of the oil after the citral is removed. This oil, after being dried over calcium chloride, can be distilled into five fractions under 25 mm. pressure: (1) 90— 100° , 49%; (2) 100— 120° , 5%; (3) 120— 130° , 9%; (4) above 130° , 6%; (5) residue, 31%. From the first fraction they have isolated a substance which they have named *perillen*, b. p. 185— 186° , D 20 0.9017, n_D^{21} 1.47053, $[\alpha]_D$ zero. Analysis gives the empirical formula $C_{10}H_{14}O$. There are only a few substances known to occur in plants having a similar composition, the best known being carvone and myrrol. *Perillen* differs from the former in b. p. and odour, and from the latter by the fact that the purple colour with bromine quickly changes to green. It contains one furan nucleus, one methyl group, and one side-chain with one double bond, which on oxidation yields $CH_2Pr^\beta \cdot CH_2 \cdot CO_2H$. The annexed formula is suggested for this new oil. *Dihydroperillen* is obtained by reducing *perillen*, b. p. 182° , D 22 0.8852, n_D^{22} 1.45762. From the remaining fractions there was obtained a compound, b. p. 251° , D 21 0.9088, n_D^{21} 1.50176, $[\alpha]_D$ -4.358°, which is concluded to be a sesquiterpene.



CHEMICAL ABSTRACTS.

Uzarin from Gomphocarpus Root. LUDWIG KOFLER (*Arch. Pharm.*, 1917, **255**, 550—552).—Uzarin (compare Hennig, A., 1918, i, 94) may be readily obtained by extracting the root known as *Gomphocarpus spec.*, or Wasicky's ithongua (*Ber. deut. Pharm. Ges.*, 1916, **26**, 267), with methyl alcohol on the water-bath, evaporating the alcohol, treating the residue with boiling water, filtering the hot solution, and recrystallising the uzarin which separates on cooling, first from a mixture of methyl alcohol and ether, and afterwards from boiling water. The percentages of uzarin obtained in this way from the two products were 4.84 and 3.70 respectively. Uzarin has a slightly bitter taste, and is pre-

precipitated from aqueous solution by tannic acid, excess of which redissolves the precipitate. Various colour reactions of the glucoside are described. It begins to decompose at 190° . T. H. P.

Meconic Acid and its Behaviour in the Estimation of Morphine in Opium. A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, 255, 482—496).—Ammonium meconate separates in crystals containing $1\text{H}_2\text{O}$ when prepared in aqueous solution or in the anhydrous form, $(\text{NH}_4)_2\text{C}_7\text{H}_2\text{O}_7$, when prepared from meconic acid and ammonium acetate in absolute alcoholic solution; the salts are neutral towards iodeosin and dimethylaminoazobenzene. Calcium meconate has the formula $\text{C}_7\text{H}_2\text{O}_7\text{Ca}$, or, when dried at 110° , $\text{C}_{14}\text{H}_2\text{O}_{13}\text{Ca}_2$, both salts being neutral towards the above indicators; the solubility of the former in *N*/10-ammonia solution was measured at 18° .

The meconic acid contained in opium does not affect the results obtained in estimating the morphine by precipitation with ammonia (compare this vol., ii, 437). T. H. P.

Physiologically Active Constituents of Certain Philippine Medicinal Plants. III. A. H. WELLS (*Philippine J. Sci.*, 1919, 14, 1—7).—The dry wood of *Arcangelisia flava* (Linn.) contains 4.8% of berberine, probably a higher percentage than that in any other Philippine plant. As the wood is soft and porous and contains but little extractive matter, the recovery of the alkaloid is simple, involving merely maceration with 95% alcohol, evaporation of most of the alcohol, and the recrystallisation of the salt formed by the addition of a mineral acid to the concentrated liquor. The plant is therefore an excellent source of the drug. *Cassia siamea* (Lam.) occurs only in cultivation as a shade tree. The pods, leaves, and branches contain a poisonous alkaloid having the empirical formula $\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$. The rhizomes of *Geodorum nutans* contain about 14% of a water-soluble adhesive gum of exceptional strength and lasting power. *Coriaria intermedia*, known in New Zealand as "toot plant," contains small quantities of a poisonous glucoside in its leaves and fruit. G. F. M.

Syntheses in the Cinchona Series. I. The Simpler Cinchona Alkaloids and their Dihydro-derivatives. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, 41, 817—833).—The reduction products of various cinchona alkaloids and certain synthetic homologues of these products are described. The reduction of cinchonine, cinchonidine, quinine, and quinidine to hydrocinchonine, hydrocinchonidine, hydroquinine, and hydroquinidine was readily effected by means of palladous chloride in dilute sulphuric acid solution (D.R.-P. 252136). The properties of the hydrogenated alkaloids obtained agree with those recorded for the natural compounds. Hydrocupreine may be prepared in large quantity by de-etherifying hydroquinine by means of boiling aqueous hydrobromic acid.

Hydrocupreine and its ethyl ether, which, as derivatives of hydro-

quinine, are lævorotatory, are compared with the corresponding dextrorotatory stereoisomerides derived from hydroquinidine. These, which are named hydrocupreidine and ethylhydrocupreidine, have not been previously described, although the former was evidently obtained crystalline by Forst and Böhringer (A., 1882, 1306) by heating hydroquinidine with hydrochloric acid in a sealed tube. Hydrocupreidine is readily isolated from hydroquinidine by the method used for preparing its lævorotatory isomeride, hydrocupreine, and it is easily converted into its ethyl ether by means of ethyl sulphate and alcoholic alkali.

Quinicine was prepared by isomerisation of quinidine in accordance with Miller, Rohde, and Fussenegger's instructions (A., 1901, i, 95), and was readily isolated in good yield as the monohydrochloride, which was unobtainable by other workers.

sec-Octylhydrocupreine dihydrochloride, recommended in Germany during the war, under the name "Vuzin," for the treatment of infected wounds, has also been prepared by the authors.

The values given for the optical rotations are calculated from the formula $[\alpha] = 100\alpha/lc$, c representing grams of substance per 100 c.c. of solvent; for low concentrations, these values are close approximations to the true ones.

The properties of the anhydrous hydrochlorides of the bases are as follows: cinchonine, softens at 175° , m. p. $217-218^\circ$ (slow decomp.), $[\alpha]_D^{20} + 177.4^\circ$ ($c=1.083$); cinchonidine, softens at about $160-170^\circ$, m. p. 242° (slow decomp.), $[\alpha]_D^{20} - 117.6^\circ$ ($c=1.214$); quinine, melts to a jelly at $154-160^\circ$, $[\alpha]_D^{20} - 149.8^\circ$ ($c=1.322$); quinidine, m. p. $258-259^\circ$ (decomp.) with previous darkening and sintering, $[\alpha]_D^{20} + 200.8^\circ$ ($c=1.3$); hydroquinidine, m. p. $206-208^\circ$, $[\alpha]_D^{21} - 123.9^\circ$ ($c=1.113$); hydrocinchonidine, m. p. $202-203^\circ$, $[\alpha]_D - 89.4^\circ$ ($c=1.197$).

Hydrocupreine, prepared as described above, forms faintly cream-coloured plates, and at $185-190^\circ$ swells and evolves gas, with formation of an adherent, glassy mass, which liquefies completely and darkens at 230° ; $[\alpha]_D^{21} - 148.7^\circ$ ($c=1.13$) (compare Giemsa and Halberkann, this vol., i, 33). The *hydrochloride*, $C_{19}H_{24}O_2N_2.HCl$, forms anhydrous, radiating masses of needles, blackening at above 255° , m. p. 280° (decomp.; rapid heating), $[\alpha]_D^{20.5} - 132.3^\circ$ ($c=0.945$). The dihydrobromide ($+2H_2O$) forms leaf-like aggregates of irregular prisms; the anhydrous salt turns yellow and softens to a jelly at about $180-190^\circ$, gradually liquefying at higher temperatures. The nitrate forms rosettes of anhydrous, flat needles, m. p. $220-222^\circ$ (darkening).

Ethylhydrocupreine hydrochloride (compare Giemsa and Halberkann, *loc. cit.*) forms anhydrous, rhombic crystals melting at $252-254^\circ$ to a brown, turbid liquid, which rapidly clears, $[\alpha]_D^{21} - 123.6^\circ$ ($c=0.959$). The hydrobromide forms aggregates of anhydrous rhombs, m. p. $258-259^\circ$ (darkening), the dihydrobromide ($+0.5H_2O$), greenish-yellow crusts of rhombic crystals, and the methiodide, glistening, pale yellow plates, m. p. $195-196^\circ$, $[\alpha]_D^{21.5} - 113.0^\circ$ ($c=0.992$).

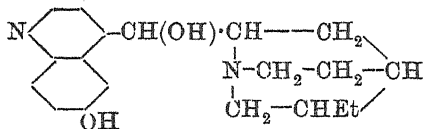
sec-Octylhydrocupreine dihydrochloride ("vuzin") forms pale

yellow sheaves and rosettes of slender needles ($+2\text{H}_2\text{O}$); the anhydrous salt softens slightly above 140° , melts to a jelly at $157\text{--}160^\circ$, and liquefies completely at $190\text{--}195^\circ$ (evolution of gas).

Hydrocinchonine hydrochloride was prepared (1) from the alkaloid occurring naturally as a by-product in the oxidation of commercial cinchonine to cinchotene, and (2) from the base prepared by reducing cinchonine by means of palladium and hydrogen. Both salts ($+2\text{H}_2\text{O}$) conformed to Forst and Böhlinger's description (A., 1881, 620). Anhydrous salt (1) darkens above 180° , m. p. $220\text{--}221^\circ$, $[\alpha]_D^{25} + 155.2^\circ$ ($c=0.796$), whilst (2) darkens slightly above 200° , m. p. $221\text{--}223^\circ$ (evolution of gas), $[\alpha]_D^{25} + 159.3^\circ$ ($c=0.741$) (compare von Arlt, A., 1899, i, 962).

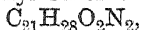
Hydroquinidine hydrochloride (compare Forst and Böhlinger, A., 1882, 1306) darkens at about 270° and decomposes at $273\text{--}274^\circ$, $[\alpha]_D^{25} + 183.9^\circ$ ($c=1.278$).

Hydrocupreidine (annexed formula) forms glistening, cream-coloured, hexagonal plates ($+0.5\text{--}1\text{H}_2\text{O}$); the anhydrous base softens to a jelly above 170° and liquefies completely at about 195° , $[\alpha]_D^{19.5} + 253.4^\circ$ (in alcohol; $c=1.422$). In its chemical properties it is strictly analogous to its lævorotatory stereoisomeride.



The *hydrochloride*, $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}\cdot\text{H}_2\text{O}$, forms rosettes and sheaves of prismatic needles, and, when anhydrous, has m. p. $231\text{--}233^\circ$ (darkening), $[\alpha]_D^{25} + 194.2^\circ$ ($c=0.618$); its aqueous solution is yellow. The *dihydrobromide* forms anhydrous, pale yellow, glistening plates, and turns yellow when heated, but does not melt at 275° . The *hydriodide* forms pink, rhombic plates ($+\text{H}_2\text{O}$), m. p. $209\text{--}212^\circ$ (anhydrous). The *nitrate* forms cream-coloured rhombs ($+\text{H}_2\text{O}$), the anhydrous salt turning yellow and softening to a jelly at about 160° , and liquefying completely at $175\text{--}180^\circ$. The *methiodide* forms glistening prisms, m. p. about 295° (decomp.), $[\alpha]_D^{20} + 202.6^\circ$ (in 50% alcohol; $c=0.555$).

Ethylhydrocupreidine (ethyl ether of hydrocupreidine),



forms rosettes and sheaves of slender needles, m. p. $197.5\text{--}198^\circ$, showing slight preliminary softening and resolidifying a few degrees below the melting point; $[\alpha]_D^{25} + 212.8^\circ$ (in alcohol; $c=1.008$). The *hydrochloride* forms nacreous aggregates of flat needles and long, narrow plates ($+4\text{H}_2\text{O}$) with a slightly bitter taste; the anhydrous salt sinters to a jelly at $140\text{--}155^\circ$, m. p. $258\text{--}260^\circ$, $[\alpha]_D^{25} + 183.3^\circ$ ($c=0.592$). The *hydrobromide* forms anhydrous, rhombic crystals, m. p. $250.5\text{--}253^\circ$ (slow decomp.). The *dihydrobromide* forms radiating masses of slender, silky needles ($+0.5\text{H}_2\text{O}$), the dried salt turning yellow above 130° , melting to a jelly at about $175\text{--}185^\circ$, and swelling and evolving gas at $200\text{--}205^\circ$. The *methiodide* forms rhombs and prisms, decomposing at $253\text{--}255^\circ$, $[\alpha]_D^{25} + 189.6^\circ$ (in methyl alcohol; $c=1.131$).

Quinicine hydrochloride, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2\cdot\text{HCl}$, which may readily be

prepared directly from the base, forms arborescent aggregates of minute leaflets, m. p. (1) 179—180°, (2) 180—182°, $[\alpha]_D^{25}$ (1) +16.26° ($c=0.80$), (2) +13.7° ($c=1.861$). T. H. P.

Stereochemistry of Hyoscine. HAROLD KING (T., 1919, 115, 974—982).

Preparation of 6-Hydroxy-2-phenylpyridine-5-carboxylic Acid. CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 312098; from *Chem. Zentr.*, 1919, ii, 852).—The process depends on the oxidation of 2-phenylquinoline bases, substituted in the benzene nucleus, by potassium permanganate in acid solution. Examples are cited of the oxidation of 8-methoxy-2-phenylquinoline, 8-hydroxy-2-phenylquinoline, 6-ethoxy-2-phenylquinoline, m. p. 132° (prepared by heating the corresponding 4-carboxylic acid at 250°), and 6-amino-2-phenylquinoline, m. p. 122—123° (prepared by heating the corresponding 4-carboxylic acid above its melting point). 6-Hydroxy-2-phenylpyridine-5-carboxylic acid (2-phenylpyridone-5-carboxylic acid) forms colourless crystals, m. p. 280—281° (corr.), 287—288° when rapidly heated, and is transformed at 300° into 2-phenylpyridone. A sulphonic acid is produced when it is treated with sulphuric acid containing 15% of SO_3 at 150—160°. The aqueous solutions of the alkali salts are slightly fluorescent. The acid is used medicinally. 6-Hydroxypyridine-2:5-dicarboxylic acid, m. p. 287—289° (decomp.), is obtained as a by-product during the oxidation of 8-methoxy-2-phenylquinoline. H. W.

Dyes Derived from Quinolinic Acid. PRAPHULLA CHANDRA GHOSH (T., 1919, 115, 1102—1105).

Crystallography and Optical Properties of Pinaverdol. EDGAR T. WHERRY and ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1919, 9, 396—405).—Pinaverdol, or 1:1':6'-trimethylisocyanine iodide, is used as a sensitising dye for photographic plates. The crystals are monoclinic ("peri-rhombic") with $a:b:c=1.1014:1:1.6053$, $\beta=88^\circ 20'$, and they vary from prismatic to tabular in habit in different preparations. They display brilliant reflection pleochroism with metallic colours; faces in the prism-zone are brass-yellow, whilst those nearly perpendicular to the vertical axes are bronze-violet; faces lying between these display intermediate colours, usually a brilliant metallic-green (beetle-green). Crystals less than 0.02 mm. in thickness transmit light and show strong absorption and pleochroism. Refractive indices, α about 1.58, β and γ more than 1.75, probably near 2.0; optically negative.

L. J. S.

Isolation of the Iodine Compound which Occurs in Thyroid. E. C. KENDALL (*J. Biol. Chem.*, 1919, 39, 125—147).—Hydrolysis of the fresh thyroid glands is effected with aqueous sodium hydroxide for twenty-four hours. A quantitative separation

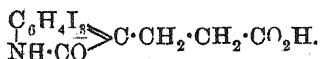
of the fats as sodium soaps is then possible, and a perfectly clear alkaline filtrate of the hydrolysed tissue is obtained. On acidification of this solution, a fine, flocculent precipitate separates which contains approximately 26% of the total iodine. The total iodine is therefore divided into acid-soluble and acid-insoluble fractions. The proportion found in each fraction is remarkably constant, and it is suggested that the ratio expresses the equilibrium existing in the glands between the completed iodine compound possessing physiological activity and the materials which are used by the gland in the building up of this substance. When physiologically tested, the acid-soluble components are inactive, but the small acid-insoluble fraction is highly active.

This fraction apparently consists of a mixture of substances possessing the properties of colloids. As a whole, the fraction possesses acidic properties, and it was ascertained that the iodine compound was not present in the free form. By repeated precipitation with barium hydroxide and removal of the barium as barium sulphate, a preparation containing 47.3% of iodine and nearly free from coloured impurities was obtained. This material was dissolved in 95% alcohol, and on evaporation yielded a white powder insoluble in alcohol and containing about 60% of iodine. When this product was dissolved in aqueous sodium hydroxide, precipitated by adding sulphuric acid, and boiling, it was converted into fine, white, microscopic crystals. This iodine compound has been termed *thyroxin*. The experimental conditions which influence the isolation of thyroxin are fully considered. When an impure preparation of thyroxin is neutralised, iodine is eliminated, but this does not occur as readily when the pure product is used. Thyroxin is very susceptible to reduction in alkaline solution by means of metals.

There are two distinct actions produced by carbon dioxide. One is a partial purification of thyroxin by precipitation from an alkaline solution, whilst the other results in the formation of a mono-metal salt of the closed-ring form of thyroxin.

One of the most important reasons for the failure to separate thyroxin consistently was the variability of the samples of desiccated thyroid used. Samples obtained during the winter months show that during this period the glands are so low in iodine content as to make the isolation impracticable.

The process has been carried out on a large scale, and is fully described. It is stated that the substance is β -4:5:6-tri-iodo-2-keto-4:5:6-trihydroindolepropionic acid,



It may exist in three forms, a keto-form with the carbonyl group adjacent to the imino-group, the tautomeric form with an α -hydroxy-group and doubly linked nitrogen with no hydrogen in position 1, and a form in which there is an open-ring structure. It is stated that the synthesis has been accomplished by Osterberg

in 1917, and that his work has been repeated and confirmed in 1919. No details of the synthesis or of the determination of structure are given.

An acetyl derivative has been prepared. This derivative yielded a disilver salt, and to account for this, rupture of the pyrrole ring between the imino- and the carbonyl groups is assumed to have taken place.

J. C. D.

Capsaicin. I. ARTHUR LAPWORTH and FRANK ALBERT ROYLE (T., 1919, 115, 1109—1116).

Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 311906, additional to D.R.-P. 298706; from *Chem. Zentr.*, 1919, ii, 851—852. Compare A., 1918, i, 191).—Thiazole compounds are obtained by treating o-halogen-substituted acidylaminoanthraquinones with alkali sulphides in accordance with the scheme $A \begin{smallmatrix} \text{NH} \cdot \text{CO} \cdot \text{R} \\ \text{Hal} \end{smallmatrix} + \text{H}_2\text{S} \rightarrow A \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{R} + \text{H}_2\text{O} + \text{H} \cdot \text{Hal}$.

where A represents the anthraquinone group. Thus, C-phenyl-1:2-anthraquinonethiazole, pale brown needles, which yield yellow to reddish-brown solutions in organic solvents and yellowish-brown solutions in sulphuric acid, is prepared by boiling 2-bromo-1-benzoylaminoanthraquinone with alcohol and crystalline sodium sulphide. Similarly, 1-chloro-2-acetylaminoanthraquinone gives C-methylanthraquinone-2:1-thiazole, yellowish-green needles, m. p. 258°, which dissolve in organic media and sulphuric acid, forming yellowish-brown and yellow solutions respectively.

H. W.

Reaction of Iodoantipyrine. J. BOUGAULT (*Ann. Chim. anal.*, 1919, [ii], 1, 254; from *Soc. Pharm.*, 1919).—Two atoms of iodine are liberated, and antipyrine (1-phenyl-2:3-dimethyl-5-pyrazolone) is regenerated when an aqueous solution of iodoantipyrine is treated with potassium iodide and hydrochloric acid; this reaction, analogous to that given by hypoiodous amides, indicates that the iodine is combined directly with the nitrogen, although this is not confirmed by the formula ascribed to the substance.

W. P. S.

Pyrimidines. LXXXVII. Alkylation of 5-Aminouracil. TREAT B. JOHNSON and IWAO MATSUI (*J. Amer. Chem. Soc.*, 1919, 41, 782—789).—It has been shown that exhaustive alkylation by means of methyl iodide converts uracil and 5-nitrouracil ultimately into the corresponding 1:3-dimethylpyrimidines. 5-Aminouracil offers, however, greater possibilities of substitution than either of these pyrimidines owing to the presence of the basic amino-group in the 5-position of the ring. Experiment shows that the potassium salt of the aminouracil reacts with methyl iodide at the temperature of boiling methyl alcohol, yielding 5-amino-1:3-dimethyluracil, the substitution occurring entirely in the nucleus of the pyrimidine ring. That substitution does not take place in the

amino-group is established by the fact that, of the four nitrogen-substituted dimethyl derivatives possibly obtainable by alkylation with methyl iodide, neither 5-dimethylaminouracil (compare Wheeler and Jamieson, A., 1904, i, 942) nor 5-methylamino-1-methyluracil nor 5-methylamino-3-methyluracil (see below) is identical with the compound actually obtained.

In the conversion of uracil into 5-nitrouracil, the large excess of nitric acid (D 1.5) is now found to be unnecessary, a theoretical yield being obtained with 4.5 parts of the acid per 1 part of uracil.

5-Amino-1 : 3-dimethyluracil, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NH}_2$, forms hexagonal plates, m. p. 233—235°, its *hydriodide*, colourless prisms, m. p. 275°, and its *picrate*, yellow needles, melting at 246° to a dark oil with marked effervescence.

5-Methylamino-1-methyluracil, $\text{CO} \begin{smallmatrix} \text{NMe} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, obtained from 5-bromo-1-methyluracil and methylamine, forms needles, m. p. 209°, and responds to Wheeler and Johnson's test for uracil (A., 1907, ii, 826); its *picrate* crystallises in long, yellow needles, m. p. 175°.

Alkylation of 2-ethylthiol-6-pyrimidone with methyl iodide under the conditions employed by Johnson and Heyl (A., 1907, i, 728) for the preparation of 2-ethylthiol-1-methyl-6-pyrimidone, followed by hydrolysis by digestion with hydrochloric acid, yields a mixture of uracil, 1-methyluracil, and 3-methyluracil, so that alkylation occurs in both the 1- and 3-positions.

5-Bromo-3-methyluracil, prepared by Johnson and Clapp (A., 1908, i, 835) by the action of bromine on aqueous 3-methylcytosine, may also be obtained in quantitative yield by treatment of 3-methyluracil with bromine in glacial acetic acid solution at the ordinary temperature.

5-Methylamino-3-methyluracil, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, prepared by heating 5-bromo-3-methyluracil with excess of aqueous methylamine solution (33%), forms plates, m. p. 206°.

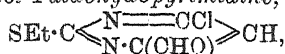
5-Methylaminouracil, $\text{CO} \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{NHMe}$, obtained by heating 5-bromouracil (1 mol.) with 33% aqueous methylamine (4 mols.) solution, forms crystals, and, when heated slowly, gradually decomposes without melting; when heated rapidly, it darkens at 285° and melts with violent effervescence at 297°. It gives Wheeler and Johnson's reaction for uracil. Its *picrate* forms stout prisms, m. p. 185° (efferves.).

An attempt to prepare 5-amino-1 : 3-dimethyluracil from 5-nitro-1 : 3-dimethyluracil by reduction with aluminium amalgam in dilute aqueous ammonia gave unsatisfactory results. T. H. P.

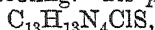
Pyrimidines. LXXXVIII. Synthesis of Cytosine Aldehyde.
TREAT B. JOHNSON and LOUIS A. MIKESKA (*J. Amer. Chem. Soc.*, 1919, 41, 810—817).—The action of phosphorus oxychloride or

pentachloride on 2-ethylthiol-4-aldehydo-6-pyrimidone (compare Johnson and Cretcher, A., 1915, i, 1002) gives, not the expected imide chloride or its chloro-ether, but 6-chloro-2-ethylthiol-4-aldehydopyrimidine. The action of ammonia on this compound results in the replacement of the chlorine atom by an amino-group, but the ammonia reacts also with the aldehyde group, giving 6-amino-4-iminomethyl-2-ethylthiolpyrimidine; hydrolysis of the latter appears to proceed beyond the formation of cytosine-4-aldehyde to the stage of complete reduction of the compound to uracil. A third product of the action of alcoholic ammonia on 6-chloro-2-ethylthiol-4-aldehydopyrimidine is the anhydro-derivative of 6-amino-2-ethylthiol-4-aldehydopyrimidine, this resulting from the inner condensation of the corresponding aldehyde. The 6-amino-2-ethylthiol-4-aldehydopyrimidine was not isolated, but it appears to represent the principal product of the reaction, and, on digestion with hydrochloric acid, is converted into cytosine-4-aldehyde with evolution of ethyl mercaptan.

6-Chloro-2-ethylthiol-4-aldehydopyrimidine,



forms a dark oil, b. p. 138—139°/10 mm., 151—158°/14 mm., solidifying completely on cooling. Its *phenylhydrazone*,



forms long, yellow needles, m. p. 147°, and its *anil*, $\text{C}_{13}\text{H}_{12}\text{N}_3\text{ClS}$, distorted prisms, m. p. 85°.

6-Amino-4-iminomethyl-2-ethylthiolpyrimidine,
 $\text{SEt}\cdot\text{C}\begin{array}{c} \text{N}=\text{C}(\text{NH}_2) \\ \text{N}\cdot\text{C}(\text{CH}\cdot\text{NH}) \end{array}\text{CH},$ forms prisms, m. p. 182°.

The inner anhydride of 6-amino-2-ethylthiol-4-aldehydopyrimidine (annexed formula) forms crystals, m. p. about 210° (decomp.).
 T. H. P.

Ricinine. E. WINTERSTEIN, J. KELLER, and A. B. WEINHAGEN (*Arch. Pharm.*, 1917, 255, 513—539).—The formula, $\text{C}_{15}\text{H}_{14}\text{O}_4\text{N}_4$, given by Soave (A., 1896, i, 386) for ricinine must be regarded as erroneous, the results of the authors' analyses and of an investigation of the decomposition products indicating the formula $\text{C}_8\text{H}_8\text{O}_2\text{N}_2$, although ebullioscopic measurements in chloroform, methyl acetate, and pyridine yield values corresponding with $\text{C}_{12}\text{H}_{18}\text{O}_3\text{N}_3$; no explanation of this discrepancy is advanced. The compound, $\text{C}_8\text{H}_8\text{O}_2\text{N}_2\cdot\text{HgCl}_2$, m. p. 201—202°, Soave (*loc. cit.*) described as $\text{C}_{17}\text{H}_{18}\text{O}_2\text{N}_2\cdot 2\text{HgCl}_2$, m. p. 204°.

Ricinine is readily hydrolysed by alkalis, yielding methyl alcohol and the sparingly soluble ricininic acid, $\text{C}_7\text{H}_6\text{O}_2\text{N}_2$, m. p. 292°; Soave gave m. p. 295°, and Maquenne and Philippe (A., 1904, i, 339; 1905, i, 80) m. p. 320°, which is that of the sodium salt. One hundred grams of water dissolve 0.072 gram of the acid at 18° and 0.87 gram at 100°. The *silver* (+ H_2O) and *barium* salts were prepared and analysed. Ricininic acid is optically inactive,

and attempts to esterify it were unsuccessful. Treatment of ricinine with a small proportion of permanganate results in hydrolysis accompanied by oxidation of the methyl alcohol liberated, whilst, when excess of permanganate is used, ammonia, hydrocyanic, oxalic, and succinic acids are formed, together with other products not investigated.

When distilled with zinc dust, ricinine gives pyridine and other compounds, and when fused with potassium hydroxide, aliphatic amines. Towards ordinary reducing agents, ricinine exhibits considerable stability, but by hydrogen in presence of platinum black it is slowly converted into tetrahydricinine, $C_8H_{12}O_2N_2$, which is far less poisonous than ricinine and forms a readily soluble, crystalline *hydrochloride*, $C_8H_{12}O_2N_2 \cdot HCl$, m. p. $212-215^\circ$, a crystalline *platinichloride*, $(C_8H_{12}O_2N_2)_2 \cdot H_2PtCl_6$, decomposing at about $222-225^\circ$, and an *aurichloride*, $C_8H_{12}O_2N_2 \cdot HAuCl_4$, sparingly soluble in water. Tetrahydricinine gives precipitates with a large number of alkaloid reagents. Hydrogenation of ricinic acid yields methylamine.

When heated with concentrated hydrochloric acid at 145° , both ricinine and ricinic acid yield ammonia and the base, $C_6H_7O_2N$ (compare Maquenne and Philippe, *loc. cit.*), which is also obtained by the action of 57.4% sulphuric acid on ricinic acid at 140° . Under the latter conditions, ricinine gives a *base*, $C_7H_9O_2N$ ($+3H_2O$), which crystallises in shining, felted needles, m. p. $55-57^\circ$ or $112-114^\circ$ (anhydrous), and yields a *platinichloride*, $(C_7H_9O_2N)_2 \cdot H_2PtCl_6$, m. p. $198-199^\circ$, an *aurichloride*, $(C_7H_9O_2N)_2 \cdot HAuCl_4 \cdot H_2O$,

m. p. $129-131^\circ$ (dried in a vacuum), and a *bromine* additive compound, m. p. 95° or 110° (dry); various reactions of this base, which exhibits normal cryoscopic behaviour in water, are described. The decomposition of ricinine by sulphuric acid is expressed by the equation $C_8H_8O_2N_2 + 2H_2O = NH_3 + CO_2 + C_7H_9O_2N$, and that of ricinic acid by $C_7H_6O_2N_2 + 2H_2O = NH_3 + CO_2 + C_6H_7O_2N$.

Both ricinine and the base, $C_7H_9O_2N$, contain one methoxy-group in the molecule; the former yields neither a benzoyl nor an acetyl compound, but with bromine it gives the *bromo-derivative*, $C_8H_7O_2N_2Br$, m. p. $226-230^\circ$ (compare Evans, A., 1900, i, 309; Soave, *loc. cit.*). Ricinic acid cannot be converted into ricinine by the ordinary methods of methylation.

Since, under certain experimental conditions, ricinine gives Weidel's and the murexide reactions, it is possible that its molecule contains a pyrimidine ring.

T. H. P.

Vicine. I. E. WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1919, 105, 258-264. Compare Levene, A., 1914, i, 1004).—The author's preparation had m. p. $239-242^\circ$ (decomp.). A 10% solution in 10% sulphuric acid had $[\alpha]_D^{25} = -8.77^\circ$, whilst a 6.6% solution in *N*/5-sodium hydroxide gave $[\alpha]_D = -12.1^\circ$. On hydrolysis with *N*-sulphuric acid, it yielded 59.3% and 60.05% of a sugar,

identified definitely as dextrose. The elementary analysis corresponded with $C_{10}H_{16}O_7N_4$. J. C. D.

Abnormal Behaviour of Glyoxalinecarboxylic Esters and Anilides towards Diazonium Salts. ROBERT GEORGE FARGHER and FRANK LEE PYMAN (T., 1919, 115, 1015—1020).

Partition of the Benzene Derivatives and the Benzene Carbon in the Protein Molecule. E. and H. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1919, 105, 242—248).—An attempt to gain information as to the partition of the cyclic amino-acids in proteins by a study of their degradation products formed during putrefaction. From putrefied fibrin there were isolated 1.26% of indole, either in the free form or as indoleacetic acid, 2.85% of phenol, free or as hydroxy-acids, and 1.27% of β -phenylpropionic acid. A study of these quantities throws light on the amounts of tyrosine, tryptophan, and phenylalanine originally present in the fibrin, and it is suggested that such studies might be of value in determining the biological value of proteins. J. C. D.

Preparation of Protein Free from Water-soluble Vitamine. THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and EDNA L. FERRY (*J. Biol. Chem.*, 1919, 39, 35—46).—The persistence with which the water-soluble vitamine is retained by edestin suggests that it is chemically combined therewith. Caseinogen, lactalbumin, gliadin, and ovovitellin as prepared by the usual methods do not appear to carry this vitamine as an impurity. The water-soluble vitamine present in yeast is not entirely destroyed by digestion with 0.1*N*-sodium hydroxide for twenty-one and a-half hours, followed by heating on the water-bath for two hours. J. C. D.

Effect of Various Acids on the Digestion of Proteins by Pepsin. J. H. NORTHROP (*J. Gen. Physiol.*, 1919, 1, 607—612).—The rate of digestion of gelatin, egg-albumin, edestin, blood-albumin, and caseinogen by pepsin in the presence of hydrochloric, nitric, acetic, sulphuric, oxalic, phosphoric, and citric acids was followed by measuring the increase in free amino-groups by the method of Van Slyke (A., 1913, ii, 1084). The estimations were made at two ranges of hydrogen-ion concentration, $p_H=1.0$ to 1.5 and $p_H=2.5$ to 3.5. The rate of hydrolysis of all the proteins studied was found to be identical for all the acids except acetic acid. These experiments show that the physical properties of the solution, such as viscosity, have little or no effect on the rate of digestion. The simplest explanation of the results would seem to be that the rate of digestion of the protein is determined by the amount of acid protein salt formed. J. C. D.

The Proteins of Fenugreek Seeds. H. E. WUNSCHENDORFF (*J. Pharm. Chim.*, 1919, [vii], 20, 86—88).—Fenugreek seeds contain 27% of proteins; the latter consist of globulin, 25%; two albumins, 20%; and a nucleoprotein, 55%. The nucleoprotein is rich in iron (3.99%) and phosphorus (1.58%); on hydrolysis with

10% hydrochloric acid for two hours at 100°, it yields alanine 1·6%, leucine 2·50%, phenylalanine 2·5%, glutamic acid 35·71%, aspartic acid 1·32%, tyrosine 4·65%, arginine 3·15%, histidine 0·75%, proline 3·80%, glycine and lysine none. A solution of the substance in alkali hydroxide has $[\alpha]_D -97\cdot7^\circ$.

W. P. S.

Salmine. MATHILDE NELSON-GERHARDT (*Zeitsch. physiol. Chem.*, 1919, **105**, 265—282).—The author has found that there is an increase in acidity on hydrolysis of salmine similar to that observed by Goto in the hydrolysis of clupeine (*A.*, 1903, i, 303). The cause of this increase is discussed. Sørensen's explanation ("Ergebnisse der Physiologie," 1912), based on the keto-enol tautomerism of the peptide linkings, demands that the original acidity returns when all these linkings are broken. This theory holds in the case of certain examples, such as glycine anhydride and leucylglycine. If it is to apply to the hydrolysis of salmine, it is necessary to assume that the process ceases before all the peptides are resolved. On investigation, peptides of the monoamino-acids were found to be present, and when the hydrolysis was completed by decomposition of these complexes, the acidity returned to the original value.

There is, however, evidence of another cause of increased acidity. Search for a new dibasic monoamino-acid was unsuccessful. Other possible causes are considered.

J. C. D.

Bacterial Catalase. III. MARTIN JACOBY (*Biochem. Zeitsch.*, 1919, **95**, 124—130).—The preparation of a highly active catalase fraction from *Bacillus proteus* is described.

J. C. D.

Studies on Lipase. GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 387—422).—On account of discrepancy among various workers on the question of relationship between acid and lipase, the authors conducted extensive studies on (1) the medium for the lipolytic enzyme, (2) optimum concentrations of the different acids for activation of the zymogen, (3) the effect of washing, and (4) the effect of alcohol, water, and various other substances. This paper is partly polemical with regard to Tanaka's paper (*ibid.*, **34**, 737). Castor beans are used for the source of lipase and soja-bean oil for the substratum. The results confirm Hoyer's work that the function of acid is solely to activate the zymogen, and the activated lipase can act without the addition of any acid, but after repeated washing a little addition of an acid will accelerate the reaction. Sensitivity of activated lipase against an acid depends entirely on the amount of the oil present in the medium. If activated lipase is left in an acid without any oil and then later the oil is added, no hydrolysis will take place, whereas if the oil and the enzyme are put together from the beginning, the hydrolysis will occur even to the extent of 80%. The optimum concentration of various acids for activation varies according to the kind of acid used, the stronger acids requiring fewer c.c. of normal solution than weaker acids, but the extent of hydro-

lysis is always greater with the weaker acid. Using 2.5 grams of the castor beans + 25 grams of the oil + 5 c.c. of water (including c.c. of the acid used), incubating at 39° for three hours, the amount of *N*-nitric acid necessary to give the maximal hydrolysis (32.9%) is 0.6 c.c.; for *N*-sulphuric acid, 0.75 c.c. The maximal digestion being 37%; for *N*-oxalic acid, 0.75 c.c., giving 36.8%; 0.75 c.c. of *N*-tartaric acid gives 41.8%; 1 c.c. *N*-lactic acid, 41.5%; 1.5 c.c. *N*-citric acid, 56.2%; 4 c.c. of *N*-succinic acid, 45.97%; and 3 c.c. of *N*-acetic acid, 54.4%. In making a permanent lipase preparation, the optimum amount of acids should be added according to (1) the amount of the oil the seed contains, the greater the amount of the oil the smaller the number needed; (2) the size of the crushed beans, the smaller the granules the less the amount of the acid needed; (3) temperature, the higher the less amount of acid; and (4) time, the longer the treatment the less the acid necessary. Dilution of the acid, maintaining in the medium the absolute amount of the acid necessary for the maximal amount of hydrolysis, lessens the lipolytic power, especially in the case of strong acids. The strong acids once used for activation of zymogen will have no effect for activating a new bean, but the weak acids will. When the castor bean is washed with water containing sodium or calcium chloride, its enzymic power is reduced, probably by loss of globulin. Addition of acetic acid will counteract this salt effect. Unlike other enzymes, lipase is exceedingly sensitive to alcohol, but ether, benzene, and carbon disulphide will not destroy it. Lipase in aqueous solution loses its activity very quickly if no oil is present.

CHEMICAL ABSTRACTS.

Manufacture of the Organic Phosphorus Reserve Compound of Green Plants, and Salts Thereof. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat., 130456).—A pure sodium salt of the organic phosphorus reserve compound is prepared from the impure material through the intermediate precipitation of the ferric salt, its decomposition by sodium hydroxide, and the addition of alcohol to the filtered solution. The crystalline mass which separates gives on recrystallisation from water efflorescent prisms of the composition $C_6H_6O_{24}P_6Na_{12} \cdot 47H_2O$, m. p. 49°. The anhydrous salt is a stable, white, non-hygroscopic powder, alkaline in reaction and insoluble in organic solvents. Pure alkaline earth, lead, and copper salts are obtained by double decomposition, and from them the pure acid of the phosphorus compound is prepared by the action of oxalic acid or hydrogen sulphide, as the case may be. [See, further, *J. Soc. Chem. Ind.*, 1919, 739A.] G. F. M.

Cytidine-Phosphoric Acid. P. A. LEVENE (*J. Biol. Chem.*, 1919, 39, 77—81. Compare A., 1918, i, 138).—The preparation of the pure brucine salt of cytidine-phosphoric acid is described. From this may be prepared the barium salt, $C_8H_{12}O_8N_3PBa$. The optical rotation of the air-dried substance was $[\alpha]_D^{20} + 14.0^\circ$. By hydrolysis of the barium salt by heating with 10% sulphuric acid

in a sealed tube at 125°, cytidine was formed, where cytosine had been expected. No explanation of this result is given. No uridine was found in the mother liquors from the cytidine picrate.

J. C. D.

Sodium Inositol-hexaphosphate (a Correction). S. POSTERNAK (*Compt. rend.*, 1919, 169, 337—338. Compare this vol., i, 426).—A stable form of this compound containing only 35 mols. H₂O is slowly deposited from concentrated solution at about 20°. It melts at 58—59° and loses water of crystallisation at 120°, and the crystallographic measurements recently given (this vol., i, 426, 433) refer to this substance and not to the efflorescent hydrate containing 44 mols. H₂O.

G. F. M.

Substituted Phenylarsinic Acids and their Reduction Products, and the Estimation of Arsenic in such Compounds. ROBERT GEORGE FARGHER (*T.*, 1919, 115, 982—992).

Formaldehyde Derivative of Arsenophenylglycine. K. J. OECHSLIN (U.S. Pat. 1299214).—Arsenophenylglycine is dissolved in a 6% solution of sodium carbonate and treated with formaldehyde. On the addition of alcohol or acetone to the solution, a sodium salt of the reaction product is obtained, which possesses a light yellow colour, and may be dried and kept in the air for some time without decomposition.

CHEMICAL ABSTRACTS.

Acetylarsenophenylglycine. K. J. OECHSLIN (U.S. Pat. 1299215).—A solution of acetylphenylglycinearsinic acid (50 grams) and sodium hyposulphite (500 grams) in water (2500 c.c.) is heated for two hours at 45—55°, and acetic acid (70 c.c.) is then added. Acetylarsenophenylglycine is precipitated in light yellow flakes. Acetylarsenophenylglycine also may be prepared by dissolving arsenophenylglycine in sodium carbonate solution and successively adding acetic anhydride and hydrochloric acid.

CHEMICAL ABSTRACTS.

Physiological Chemistry.

Absorption of Light by Neutral Solutions of Oxyhæmoglobin. PAUL HÁRI (*Biochem. Zeitsch.*, 1919, 95, 257—265).—The absorption of light by neutral solutions of blood or of oxyhæmoglobin is very little different from that of solutions in aqueous sodium carbonate. The difference is attributed to the presence of small amounts of methæmoglobin.

J. C. D.

Behaviour of Inulin in the Animal Body. II. Inulin in the Alimentary Canal. RUTH OKEY (*J. Biol. Chem.*, 1919, 39, 149—162).—Inulin is hydrolysed in vitro by hydrochloric acid of a concentration approximately the same as that in the normal gastric juice provided a sufficiently long period of hydrolysis is allowed. During the time normally occupied by food in the stomach, the amount of hydrolysis is comparatively small. The presence of an enzyme capable of producing a reducing sugar from inulin has been demonstrated in sterile extracts of three samples of human faeces from radically different types of diet. Negative results were obtained with samples from a dog and guinea-pigs.

J. C. D.

Genesis of Thiocyanic Acid in Animals. VII. From what Substances is Normal Thiocyanic Acid Derived in Animals? SERAFINO DEZANI (*Arch. Farm. speriment. sci. aff.*, 1918, 26, 257—273; from *Chem. Zentr.*, 1919, iii, 65. Compare this vol., i, 423).—The negative results obtained with amino-acids and derivatives of purine in the case of the dog are in contrast with the positive results of Willanen (*A.*, 1906, ii, 784) in the case of the rabbit. The latter experiments have been repeated, particular attention being given to the influence of the nourishment. No increase in thiocyanic acid could be detected after administration of glycine, asparagine, guanine, or creatinine; evidence in favour of the hypotheses of Nencki and of Bruylants is therefore not obtained.

H. W.

Quinine and Hydroquinine in the Human Body. Behaviour of Quinine towards Red Blood Cells. J. HALBERKANN (*Biochem. Zeitsch.*, 1919, 95, 24—45).—The fate of these two substances in the body is discussed. It is shown that quinine may be taken up and retained by the erythrocytes.

J. C. D.

Presence of Histamine (β -Iminazolyethylamine) in the Hypophysis Cerebri and Other Tissues of the Body and its Occurrence Among the Hydrolytic Decomposition Products of Proteins. JOHN J. ABEL and SEIKO KUBOTA (*J. Pharm. Expt. Ther.*, 1919, 13, 243—300).—The experimental findings support the view previously expressed (*Proc. Nat. Acad. Sci.*, 1917, 3, 507—517) that the oxytoxic principle of the hypophysis is not a hormone or substance specific to this organ, but is a rather widely distributed substance, everywhere the same, which may have its origin in the various tissues or in the gastric or intestinal mucosa, or may be absorbed as such from among the products of digestion. This substance is now believed to be histamine, a substance which stimulates plain muscle in minute doses and which depresses the circulation and causes a shock-like prostration when administered in doses which lie beyond the limit of toleration. The base was isolated with certainty from pituitary tissue and gastric and intestinal mucosa of the dog, and its presence in liver tissue and striated muscle was detected. The amine was also found in erepton (com-

pletely digested meat), Witte's peptone, and amongst the products of hydrolysis of pure proteins with hydrochloric acid. It is suggested that histamine plays an important rôle as a stimulant for the gastric and intestinal musculature and as a dilator of capillaries during digestion. J. C. D.

[Physiological Action of] Optical Isomerides. V. The Tropeines. A. R. CUSHNY (*J. Pharm. Expt. Ther.*, 1919, 13, 71—93. Compare A., 1909, ii, 420).—Atropine is twenty times as strong as *d*-hyoscyamine in affecting the terminations of the chorda tympani in the dog. Therefore *l*-hyoscyamine would have an action forty times as great as that of its optical isomeride. The difference between the effects of atropine and *d*-hyoscyamine on cardiac inhibition is of the same order as on salivary secretion. The physiological action of a number of tropeines has been examined. Tropine itself is devoid of typical atropine action, but many tropeines, especially those which contain a benzene nucleus, show the characteristic effects. This is particularly intensified where there is a hydroxyl group or an asymmetric carbon atom in the side-chain. The most powerful action is shown by members of this type which contain an acid of the benzene series, together with a hydroxyl group and asymmetric carbon atom in the side-chain, and the whole molecule of which is laevorotatory. J. C. D.

Vitamine Studies. IV. Antineuritic Properties of Certain Physiological Stimulants. R. ADAMS DUTCHER (*J. Biol. Chem.*, 1919, 39, 63—68).—Thyroxin (the active principle of the thyroid), desiccated thyroid, pilocarpine, and tethelin apparently produced definite relief in certain acute cases of avian polyneuritis. The response was not, however, of the type obtained when vitamine preparations were given. J. C. D.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of *Bacillus Acetoethylicum* with Reference to the Formation of Acetone. JOHN H. NORTHROP, LAUREN H. ASHE, and JAMES K. SENIOR (*J. Biol. Chem.*, 1919, 39, 1—21).—The description of an organism termed *Bacillus acetoethylicum* which was isolated from old potatoes is given. The organism resembles in some ways the *B. macerans* described by Schardinger (*Centr. Bakt. Par.*, 1905, ii, 14, 772), but it is not thought that the two are identical. This organism produces acetone and ethyl alcohol from starch or sugar. The optimum conditions for the fermentation have been studied, and a semi-continuous method for carrying on the process is described. [See, further, *J. Soc. Chem. Ind.*, 1919, October.] J. C. D.

Formation of Acids by Moulds and Yeast. III. FRIEDRICH BOAS and HANS LEBERLE (*Biochem. Zeitsch.*, 1919, **95**, 170—178. Compare *ibid.*, 1918, **90**, 78; **92**, 171).—When both ammonium sulphate and acetamide are present as sources of nitrogen for *Aspergillus niger* growing in an artificial culture solution, only the ammonium sulphate is utilised, notwithstanding that acetamide would from some point of view appear a more suitable material for protein synthesis, particularly as its utilisation does not necessitate the liberation of a toxic substance, such as the sulphuric acid liberated in the utilisation of ammonium sulphate. From similar tests with glycine and acetamide, it would appear the glycine is utilised, whereas the amide is almost untouched. Experiments in which the mould has a choice between ammonium sulphate and peptone show that preferential utilisation of the former source of nitrogen occurs. In fact, when *A. niger* is given the choice between two sources of nitrogen, one of which is an ammonium salt and a strong mineral acid, it utilises the ammonium salt alone, in spite of the fact that this leads to a rise of hydrogen-ion concentration with all its deleterious consequences.

Apparently the degree of dissociation of the ammonium salt is an important factor. J. C. D.

The Formation of Soluble Starch in Relationship to Selective Nitrogen Metabolism. FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1919, **37**, 50—56).—It has been previously shown that soluble starch is formed from many carbohydrates by *Aspergillus niger* when the hydrogen-ion concentration has attained a certain value. The author has based a method of studying selective nitrogen metabolism on this observation; thus, for instance, when in a sugar solution ammonium chloride is consumed in addition to amino-acids, the hydrogen-ion concentration rapidly increases in consequence of the liberation of the greatly dissociated hydrochloric acid, so that favourable conditions are developed for the formation of soluble starch, which can readily be detected by the iodine test. The following groups have been studied: mixtures of ammonium salts (ammonium chloride and ammonium phosphate or citrate); amino-acids and peptones in the presence of ammonium chloride; acid amides (carbamide) and ammonium chloride. The latter differs from all the other sources of nitrogen which were investigated in that it is strongly dissociated. Experiments show that in mixtures of nitrogenous substances with varying degrees of dissociation, the magnitude of the latter determines the absorption into the cell. In comparison, the solubility of the substance in lipoids has but little influence. The more strongly dissociated source of nitrogen is invariably utilised even when powerfully poisonous products are thereby developed, and when other non-poisonous, lipid-soluble and suitable sources of nitrogen are present. Absorption is not regulated by the mould, but occurs exclusively according to physico-chemical properties. From the biological point of view, the mould invariably utilises the worse source of nitrogen. H. W.

Parallel Formation of Carbon Dioxide, Ammonia, and Nitrate in Soil. P. L. GAINES (*Soil Sci.*, 1919, 7, 293—311).—In laboratory experiments, purified air was drawn in a downward direction through a column of loam soil supported in a cylinder, and then through glass beads moistened with a solution of sodium hydroxide, and afterwards through glass beads moistened with dilute acid. Usually, six of these apparatus were connected in series. Estimations of the carbon dioxide and ammonia retained by the absorption vessels determined the amounts of these gases given off, and after each experiment the top layer of soil was removed and examined for ammonia and nitrates. The carbon dioxide in the soil was not taken into consideration. One per cent. of cotton-seed meal was added to the soil as a substance readily decomposed by bacteria. Observations on variation in the moisture content of the soil showed that this factor had little effect on the carbon dioxide evolved provided the amount of water was above a minimum of 12 c.c. per 100 grams of soil. The maximum amount of carbon dioxide was produced during the second day. The production of ammonia ran parallel with that of carbon dioxide, except that the optimum minimum of moisture was rather higher. The accumulation of nitrates did not begin until the fifth day, and the amount increased regularly with a corresponding diminution in that of the ammonia. Variations in air supply had a marked effect on bacterial activity. Unless the current of air was continuous, there was a distinct diminution and delay in the changes produced. In the case of ammonia, there was a permanent diminution in amount; in the other two cases, the amount of carbon dioxide finally reached that produced in continuous aeration, whilst the amount of nitrate became inversely proportional to aeration. Experiments were made also with 1% of dried blood added to the soil. With this substance, the production of carbon dioxide was much diminished and that of ammonia relatively increased, probably due to the higher nitrogen content of the blood over the cotton-seed meal and to the amount of readily oxidisable carbon being insufficient to supply energy for complete decomposition.

J. H. J.

Action of Capillary-active Substances on Plant Seeds. I. TRAUBE and HEDWIG ROSENSTEIN (*Biochem. Zeitsch.*, 1919, 95, 85—100. Compare Traube and Marusawa, A., 1916, i, 106).—The influence of a large number of substances on the germination and growth of seeds has been investigated. Narcotics, such as chloroform, ether, and urethane, produce a narcotic action which is in certain respects similar to the effect on the animal organism. Many substances, such as toluene, chlorobenzene, piperidine, pyridine, aniline, acetone, *isobutyl* acetate, and *isoamyl* alcohol are strongly toxic. Naphthalene and thymol vapour may hasten germination if the exposure is not too long, whilst *m*-cresol may in certain concentrations beneficially influence the growth of barley.

The higher fatty acids exert a marked stimulating action on the

rate of germination, whereas the lower fatty acids in low concentrations are very poisonous.

J. C. D.

The Opposed Action, Antagonism, of Manganese and Iron on the Growth of Wheat. W. E. TOTTINGHAM and A. J. BECK (*Plant World*, 19, 359—370; from *Chem. Zentr.*, 1919, iii, 110).—Small quantities of manganese chloride are harmful to the root system and inhibit the positive action of ferric chloride. Both salts are poisonous at greater concentrations, at which the ferric chloride restricts the action of manganese chloride. Small quantities of manganese chloride induce more rapid growth of the plant, but the same antagonism is observed as with the root system. In the presence of sodium hydrogen carbonate, manganese chloride is disadvantageous to the roots and green parts even in small amounts, and distinctly poisonous at higher concentrations. Contrary to previous observations, ferric chloride encourages the growth of terminal shoots, probably on account of the alkaline nature of the nutrient solution.

H. W.

The Alkaloids in Plant Injury. O. TUNMANN (*Biochem. Zeitsch.*, 1919, 95, 164—169).—No accumulation of alkaloid was found to follow injury to the leaves of *Atropa belladonna*, L., or *Pilocarpus pennatifolius*, Lem., whether caused by animals or by artificial methods. This is not in agreement with the work of Troegele (*Diss.*, Würzburg, 1900).

J. C. D.

Nutritive Factors in Plant Tissues. II. The Distribution of the Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*J. Biol. Chem.*, 1919, 39, 29—34).—The water-soluble vitamine is present in the bulb of the onion, the root of the turnip, the leaves, stem, and roots of the beet, and the fruit of the tomato. A comparison of mature and immature plants of clover, lucerne, and timothy grass indicates that the immature plants are the richer sources of water-soluble B. The bearing of this observation on the food value of hay is discussed.

J. C. D.

Relation of Sulphates to Plant Growth and Composition. H. G. MILLER (*J. Agric. Res.*, 1919, 17, 87—102).—Pot experiments were made with three soils, one selected for its high content of sulphur, namely, 0.183%, one because it had responded to free sulphur treatment, and one because it did not respond to any sulphur treatment. The plants grown were red clover, oats, and rape. The fertilisers used were calcium and sodium sulphates and free sulphur. The last was added with calcium carbonate to the soil at the time of sowing the seed; the other two were added daily in the form of 0.02% solutions. A solution of sodium nitrate was added daily in order to provide excess of nitrogen in every case. A similar set of experiments was made in which the soil was replaced by washed sand, to which was added a sterilised extract of the soil. The weight of the crops was noted, and the content of sulphur and

nitrogen estimated. It was found in every case that enhanced growth took place as compared with the control tests, especially marked in the case of the oats and clover. As this enhanced growth took place in the sand as well as in the soil, it is concluded that the sulphates and free sulphur acted directly in the promotion of growth. In the case of clover, there was a marked increase in the nitrogen content of those plants grown in soil over those grown in sand, doubtless due to stimulation of the legume bacteria by the fertilisers added, as was evidenced by the increased root development and number of nodules in these cases. J. H. J.

Nitrogen and Other Compounds in Rain and Snow.

JACOB E. TRIESCHMANN (*Chem. News*, 1919, 119, 49).—A summary of the analyses of forty-six samples of rain and snow collected at Cornell between October 1st, 1918, and June 15th, 1919, is given. The total precipitation corresponds with 56·3 cm. of rain, and contained 572 kilos. of chlorine (944 kilos. of sodium chloride), 1·679 kilos. of sulphates as SO_3 , and 5·853 kilos. of nitrates per hectare. The phosphates only amounted to 0·0089 kilos. per hectare. Only fifteen samples contained sufficient sulphate for analysis, and eleven other samples showed the merest trace of sulphate. The highest sulphate content was 0·262 part per million, the average for the period being 0·03 part per million. Five samples showed a trace of phosphate, but only four contained sufficient for estimation. The highest content of phosphate was 0·03 part per million, the average being 0·002 part per million. The chlorine content averages 11·12 parts per million, and varies between 6·10 and 25·70 parts per million. The average of the total nitrogen was 1·046 parts per million. The free ammonia is represented by 0·407, albuminoid ammonia 0·366, nitrate 0·255, and nitrite 0·018 part per million. The total nitrogen is fairly constant, and forty-three of the forty-six determinations lie between 0·18—0·45 kilos. of nitrogen per hectare. The amount of nitrogen increased from 0·669 part per million to 1·134 parts per million from February to June, that is, an increased amount of nitrogen is supplied to the soil during the growing period. J. F. S.

Ammonia-fixing Capacity of Calcium Sulphate.

FIRMAN E. BEAR and ALBERT C. WORKMAN (*Soil Sci.*, 1919, 7, 283—291).—It has been observed that the addition of calcium sulphate to manure tends to prevent loss of ammonia. To test the nature of this reaction under simple conditions, laboratory experiments were carried out in which the manure was replaced by paper pulp, which was mixed with calcium sulphate and placed in a bottle. A solution of ammonium carbonate was poured over the pulp, giving a water content of 75%. The bottle was kept at different temperatures from 20° to 80°. A current of air freed from ammonia and carbon dioxide was drawn through the mixture in the bottle, and then through absorption vessels containing standard

acid. Observations were continued over ninety-five days, air being drawn through about daily for ten minutes at a time. The nitrogen loss without calcium sulphate was 5.6225 grams, and with calcium sulphate 1.1419 grams. More nitrogen was lost at the higher temperatures, and the proportion held back by the calcium sulphate was less at those temperatures. Under the conditions of the experiment, the chemical reaction was probably that of a simple double decomposition. [See also *J. Soc. Chem. Ind.*, 1919, 731A.]

J. H. J.

Electrical Conductivity as a Measure of the Content of Electrolytes of Vegetable Saps. DOROTHY HAYNES (*Biochem. J.*, 1919, 13, 111—123).—The causes of the low values obtained in conductivity measurements in fruit juices containing considerable quantities of organic acids are submitted to examination. These low figures are due to two principal causes, first, the action of non-electrolyte (compare Arrhenius, A., 1892, 1038), and secondly, the mutual action of salts and acids in repressing dissociation. The conclusions of Dixon and Atkins (A., 1913, i, 1422) drawn from a comparison between the juice from plant organs when pressed without previous treatment and the juice of the same organs when treated by exposure to liquid air before pressing are criticised. It is suggested that there is very little evidence for the marked differences which they assume to exist in the proportional composition of the two kinds of sap. It is further suggested that these experiments afford no evidence that the protoplasm of the cells of tissue under pressure is permeable to electrolytes to any considerable extent. A formula is advanced by means of which, in certain cases, conductivity measurements may be reduced to standard conditions.

J. C. D.

Examination of the Bark of Croton gubouga. Isolation of 4-Hydroxyhygric Acid. JOHN AUGUSTUS GOODSON and HUBERT WILLIAM BENTLEY CLEWER (T., 1919, 115, 923—933).

Action of Fluorides on Vegetation. B. Field Trials. ARMAND GAUTIER and P. CLAUSMANN (*Compt. rend.*, 1919, 169, 115—122).—As the result of field trials, using amorphous calcium fluoride as the source of fluorine, the authors find that this element increases the crop yield in certain species of plants. The calcium fluoride was applied at the rate of 55.8 grams per sq. metre to a poor, sandy soil. Increased crop yields varying from 5.2 to 58.7% were obtained with wheat, oats, carrots, potatoes, peas, beans, and poppies, whilst beet, kidney beans, and cabbage gave either no increase or a decrease. In the case of potatoes, there was no marked increase in the yield in the year of application of the calcium fluoride, but a very decided increase (58.7%) in the next year. Most of the other crops showed little, if any, residual effect in the second year.

W. G.

Organic Chemistry.

The Action of Cuprous Chloride with Compounds containing the Trichloromethyl Group. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1919, **41**, 1129—1131).—As an outcome of his work on the hydrolysis of organic haloïds and the corrosion of metals (A., 1918, i, 57), the author recommends the following procedure as a test for the presence of compounds containing the CCl_3 or CBr_3 groups. A few milligrams of the substance are placed in a stoppered vessel of 10—15 c.c. capacity, which is then filled with concentrated ammonia solution. About 0.5 gram of powdered cuprous chloride is then added, and the vessel is quickly closed to exclude air, and shaken. The deep blue colour of the cupric-ammonia complex develops in a minute or two if a trichloro- or tribromo-methyl group is present. Carbon tetrachloride behaves in the same way, but hexachloroethane does not respond to the test. J. C. W.

Preparation of Trichloroethylene from Tetrachloroethane. COMPAGNIE DES PRODUITS CHIMIQUES D'ALAIS ET DE LA CAMARGUE (Eng. Pat., 132755).—The conversion of s-tetrachloroethane into trichloroethylene may be effected by ammonia in aqueous solution provided that a sufficient time be allowed for the reaction. A mixture of equal parts of water and tetrachloroethane is treated in a vessel provided with a reflux condenser with a current of ammonia gas sufficiently violent to agitate the mass. The reaction takes place slowly in the cold, and is accelerated by heating at 60—70°; it is complete in two hours if the trichloroethylene is removed as it is formed by extracting it with an excess of ammonia gas and adjusting the temperature of the condenser in accordance with this excess. The reaction may also be conducted in an autoclave by heating two parts of tetrachloroethane with two parts of an aqueous solution of ammonia (D 0.91) at 140—170° for three hours. The use of aqueous ammonia is simpler and more economical than that of alcoholic ammonia, and the yield of trichloroethylene is 92—96% of the theoretical. J. F. B.

Vapour Pressure of Tetranitromethane. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1919, **41**, 1336—1337).—The vapour pressure of tetranitromethane has been determined by a static isoteniscopic method, previously described (A., 1910, ii, 1036), over the temperature range 40—125.7°. The following values were obtained in mm. of mercury: 40°, 26.6; 45°, 34.4; 50°, 44.2; 55°, 56.1; 60°, 70.6; 65°, 88.1; 70°, 109; 75°, 134; 80°, 164; 85°, 199; 90°, 239; 95°, 286; 100°, 339; 105°, 400; 110°, 470; 115°, 550; 120°, 640; 125°, 743; and 125.7°, 760. Using the vapour-pressure curve in the way suggested by Hillebrand (A., 1915, ii, 416), the value 13.9 is obtained for the entropy

of vaporisation divided by R at the temperature (70°) at which the concentration of the vapour is 0.00507 mol. per litre. Assuming that the vapour is normal, this would indicate slight, if any, association or abnormality in the liquid at this temperature.

J. F. S.

The Oxidation of Ethyl Alcohol by means of Potassium Permanganate. WILLIAM LLOYD EVANS and JESSE E. DAY (*J. Amer. Chem. Soc.*, 1919, **41**, 1267—1285. Compare A., 1916, i, 362).—The series of experiments described in this communication are designed to elucidate the following points: (1) the nature of the products formed when ethyl alcohol is oxidised by neutral or alkaline permanganate at different temperatures; (2) the effect of changing the temperature and altering the initial concentration of alkali, and the combined effect of varying these factors; (3) the mechanism of the oxidation. The analytical methods are fully described, and a simple apparatus is illustrated in the text by means of which clear samples of the filtrate from the oxides of manganese can be obtained without exposure to the carbon dioxide of the atmosphere. In the experiments, just sufficient of a 9.21% solution of alcohol was added to 30 grams of 100% permanganate dissolved in 1000 c.c. of various solutions of potassium hydroxide to cause reduction.

The results are reproduced in a set of curves, as follows: (A) The weights of alcohol required to reduce a constant weight of permanganate at 25° , 50° , 75° , and 100° are plotted against the different concentrations of alkali, and the curves show that beyond a concentration of about 100 grams per litre, the proportion of potassium hydroxide is immaterial, whilst up to this point both increase of temperature and increased alkalinity accelerate the reduction. (B) The quantities of the oxidation products, acetic, oxalic, and carbonic acids, given by 0.1 gram-mol. of alcohol are plotted against concentrations of alkali for the four different temperatures. In neutral solutions the sole product is acetic acid, and in the experiments at 100° it is still only acetic acid as long as the concentration of alkali is less than 0.461 gram per litre. With the increase in the amount of potassium hydroxide, however, up to the maximum effect (100 grams per litre), the production of acetic acid diminishes and that of oxalic acid and carbon dioxide increases. (C) The quantities of the three oxidation products are separately plotted against alkali concentrations for the four temperatures. With increase of temperature, it appears that the yield of acetic acid falls, and the quantities of oxalic acid and carbon dioxide increase.

Another set of curves shows the connexion between the logarithms of the quantities of acetic acid produced and the logarithms of the initial concentrations of potassium hydroxide. These curves may be reproduced by the equation $y = B/x^a$, where y is the concentration of the acetic acid, x is the concentration of the alkali, a is the tangent of the line, and B is a constant, whence $\log y = \log B - a \log x$. From the values of B and a for the four

temperatures, it is possible to calculate the maximum concentration of alkali which will still permit of a theoretical yield of acetic acid. These are as follows:

Temperature.....	25°	50°	75°	100°
KOH, grams per litre...	2.55	1.19	0.655	0.460

That is, it is possible to obtain acetic acid only, no matter what the temperature, if the concentration of alkali is kept below these limits. On the other hand, if the tangents of the acetic acid log. curves (the above values of a) are plotted against temperature, a straight line is obtained which, if continued, meets the point at which $a=0$ on an axis of Y corresponding with -25° ; this means that below this temperature the yield of acetic acid would be quantitative, no matter what the concentration of potassium hydroxide.

The mechanism of the formation of oxalic acid and carbon dioxide is discussed. The experiments support the views of other workers, namely, that the oxalic acid is not formed from acetic or formic acid, but from a derivative of acetaldehyde.

J. C. W.

The Temperature of Critical Solution of a Ternary Mixture as a Criterion of Purity of *n*-Butyl Alcohol. The Preparation of Pure *n*-Butyl Alcohol. KENNEDY JOSEPH PREVITÉ ORTON and DAVID CHARLES JONES (T., 1919, 115, 1194—1203).

The Preparation of $\alpha\beta$ -Dichloroethyl Ether. E. A. WILDMAN and HAROLD GRAY (*J. Amer. Chem. Soc.*, 1919, 41, 1122—1123).—Dichloroethyl ether may be obtained by the direct chlorination of ethyl ether (Fritsch and Schumacher, A., 1894, i, 485), but the operation is accompanied by two risks: (1) If the liquid is not well cooled at the outset, and the chlorine is admitted too rapidly, explosion may be caused by the inflammation of the ether vapour. This risk is lessened when the liquid is saturated with hydrogen chloride, and then the operation may be carried on rapidly. (2) Hydrogen chloride seems to form a super-saturated solution in ethyl ether, which may suddenly break out like a geyser; to obviate this, continuous, rapid agitation is necessary.

In order to get a pure product, b. p. $66-69^{\circ}/45$ mm., chlorination must be stopped when the density is 0.96. Starting with 800 grams of ethyl ether, this point is reached in about eighty-two hours, and the yield is about 375 grams.

J. C. W.

Action of Metallic Hydroxides and Oxides and Alkaline-earth Carbonates on Methyl Sulphates. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 169, 534—537).—The behaviour of methyl sulphate in the presence of alkali hydroxides or alkaline earth oxides, hydroxides, or carbonates, depends to a large extent on the experimental conditions.

With potassium hydroxide in equimolecular proportions in methyl-alcoholic solution, methyl sulphate gives an almost quantitative yield of potassium methyl sulphate. A similar reaction occurs with calcium or barium hydroxide in the presence of a large excess of water. On the other hand, methyl sulphate may be distilled unchanged from barium or calcium oxide. With barium or calcium hydroxides in the absence of water, the action is $\text{Me}_2\text{SO}_4 + \text{M}(\text{OH})_2 = \text{MSO}_4 + \text{Me}_2\text{O} + \text{H}_2\text{O}$.

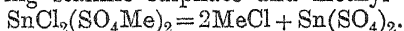
With cuprous, lead, mercuric, or silver oxides the action is, for example, $\text{Me}_2\text{SO}_4 + \text{Cu}_2\text{O} = \text{Cu}_2\text{SO}_4 + \text{Me}_2\text{O}$.

Methyl sulphate may be distilled unchanged from a small amount of an alkaline earth carbonate, but if kept at 140° for some time in the presence of the carbonate, it is decomposed according to the equation $\text{Me}_2\text{SO}_4 + \text{MCO}_3 = \text{MSO}_4 + \text{CO}_2 + \text{Me}_2\text{O}$, the reaction being slow.

W. G.

The Action of Stannic Chloride on Methyl Sulphate.

CH. BOULIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 618—620).—Stannic chloride acts on methyl sulphate in two stages, which may overlap, methyl chloride being, in each case, the gas liberated. If the action takes place at the ordinary temperature, it is represented by the equation $\text{SnCl}_4 + 2\text{Me}_2\text{SO}_4 = 2\text{MeCl} + \text{SnCl}_2(\text{SO}_4\text{Me})_2$, the methosulphate of stannyl chloride being obtained as a white, amorphous solid. At higher temperatures, this compound is decomposed, giving stannic sulphate and methyl chloride,



The use of an excess of methyl sulphate does not modify the sense of the complete reaction, but seems to favour the second stage.

The methosulphate of stannyl chloride is decomposed by aqueous potassium hydroxide, giving stannic hydroxide, potassium chloride, and potassium methyl sulphate.

W. G.

Methionic [Methanedisulphonic] Acid and its Applications in Syntheses. G. SCHROETER [with G. KOCH, G. HERZBERG, TH. MARIAM, W. SONDAG, C. FRESSENIUS, W. ROTHMANN, A. GLUSCHKE, R. VON BUTLAR-BRANDENFELS, W. DORN, DIESELHORST, E. KINDERMANN, EMMY SCHROETER, and O. CARLÉ] (*Annalen*, 1919, **418**, 161—257).—Portions of this paper have been published during the last twenty-two years.

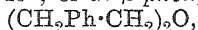
A description is given of the preparation of methanedisulphonic acid from acetylene (350—400 grams) and fuming sulphuric acid (65—70% SO_3) (about 6 kilos.) through the barium salt (700 grams of the salt from 1 kilo. of acid). The presence of phenol among the by-products, recorded by Berthelot in 1869, has been confirmed, and an explanation of its formation is suggested.

The reactions of methanedisulphonic acid have been thoroughly studied in the expectation of finding for it synthetic uses similar to those of malonic acid.

Improvements in the method of preparing methyl methanedisulphonate from the silver salt and methyl iodide (Schroeter and Herzberg, A., 1905, i, 851) are described; the ethyl ester has

been obtained in flattened needles, m. p. 28—29°. An attempt to prepare the benzyl ester from the silver salt and benzyl chloride in boiling benzene resulted in the formation of hydrogen chloride and diphenylmethane, the silver salt acting (so also does silver sulphate) simply as a catalyst.

Alkyl methanedisulphonates can also be prepared from alcohols and methanedisulphonyl chloride, but the method is not a suitable one, because, unless the violence of the reaction is moderated by the presence of a suitable diluent (ethyl ether), the resulting esters decompose into methanedisulphonic acid and ethers. The tendency of alkyl methanedisulphonates to decompose into methanedisulphonic acid and ethers (Schroeter and Sondag, A., 1908, i, 497) has been utilised in the preparation of heptyl ether, b. p. 126—127°/8 mm., D^{20}_D 0.8056, from heptyl alcohol and methanedisulphonyl chloride at 145°, of *di-β-phenylethyl ether*,



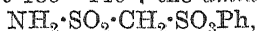
b. p. 175—176°/8 mm., D^{15}_D 1.0178 (a little styrene is also formed), from *β-phenylethyl alcohol*, and of *cyclohexene* from *cyclohexanol* in a similar manner. Aryl methanedisulphonates, on the contrary, are very stable compounds, and must be heated with a concentrated solution (50%) of alkali hydroxide to decompose them into phenols and methanedisulphonic acid. In consequence of the acidity of the methylene group between the two $\cdot\text{SO}_3\text{Ar}$ groups, the aryl esters dissolve in concentrated aqueous ammonia and in dilute solutions of alkali hydroxides. They resemble the phenols in their antiseptic and bactericidal actions. *Phenyl methanedisulphonate (methionol)*, $\text{CH}_2(\text{SO}_3\text{Ph})_2$, prepared from methanedisulphonyl chloride and phenol (4 mols.) in boiling toluene, forms colourless needles, m. p. 82°; the *sodio-* and *potassio-*derivatives, $\text{CHNa}(\text{or K})(\text{SO}_3\text{Ph})_2$, are crystalline, and the *argento-*derivative is a colourless powder. The *dibromo-*derivative, $\text{CBr}_2(\text{SO}_3\text{Ph})_2$, forms colourless crystals, m. p. 58—59°. The *o-*, *m-*, and *p-tolyl* esters, $\text{CH}_2(\text{SO}_3\cdot\text{O}\cdot\text{C}_7\text{H}_7)_2$, form crystals, m. p. 84°, 56°, and 84° respectively, whilst the *guaiacol* and *catechol* esters have m. p. 90° and 190° respectively.

Methanedisulphonyl chloride (Schroeter and Sondag, *loc. cit.*) has been obtained in two modifications. The liquid form usually obtained, m. p. 8°, D^{15}_D 1.831, is converted under conditions which have not yet been definitely ascertained into a second modification, long needles or prisms, m. p. 36—37°; the liquid form is converted into the solid by inoculation with the latter, and the solid form is converted into the liquid by warming above the m. p.

Methanedisulphonyl chloride reacts abnormally with dry ammonia in chloroform solution and with diethylamine in ethereal solution, the products in both cases being, not the expected amides, but mixtures of substances the nature of which has not yet been ascertained. The reaction with aniline (4 mols.) in chloroform or benzene solution, however, is normal (Schroeter and Herzberg, *loc. cit.*). *Methanedisulphonacetanilide*, $\text{CH}_2(\text{SO}_3\cdot\text{NAcPh})_2$, m. p. 196—197°, *methanedisulphonbenzanilide*, m. p. 204—205°, *methanedisulphonmethylanilide*, colourless needles, m. p. 141.5—142.5°,

methanedisulphonethylanilide, m. p. 112—114°, *methanedisulphonanilidoethylanilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHPh})(\text{SO}_2\cdot\text{NEtPh})$, m. p. 168°, *methanedisulphonphenetidide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, m. p. 221°, and its *methyl-*, m. p. 132—133°, *ethyl-*, m. p. 141—142°, and *aceto-phenetidides*, m. p. 155°, *methanedisulphon-p-nitroanilide*, yellow needles, carbonising above 240°, and *methanedisulphondiphenylamide*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}_2)_2$, m. p. 228°, have been prepared. The preceding primary anilides are moderately strong acids forming sodium and barium derivatives and decomposing carbonates, but anilides which do not contain the NH -group are devoid of acid character, being insoluble in aqueous alkali hydroxide solution.

When a solution of phenyl methanedisulphonate in benzene saturated with ammonia is treated with an equal quantity of phenyl methanedisulphonate and the mixture is heated in a sealed tube for three hours at 130—140°, the *amide ester*,



crystals, m. p. 167°, is obtained; the same substance is also obtained by heating phenyl methanedisulphonate and carbamide in a sealed tube at 140—160°. When a solution of phenyl methanedisulphonate in benzene supersaturated with ammonia is heated in a sealed tube at 140—145°, *methanedisulphonamide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}_2)_2$, leaflets, m. p. 233°, is obtained; it forms *sodium* and *barium* derivatives and a *monobenzoyl* derivative, leaflets, m. p. 216°. *Methanedisulphonethylanilide*, $\text{CH}_2(\text{SO}_2\cdot\text{NHEt})_2$, similarly prepared by means of a benzene solution of ethylamine, forms leaflets, m. p. 143—145°.

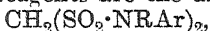
Methanedisulphonyl chloride reacts normally with esters of amino-acids in cold ethereal or chloroform solution. Thus, ethyl glycine and ethyl phenylglycine yield, respectively, *ethyl methanedisulphonaminooacetate*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 113.5°, and *ethyl methanedisulphonanilinoacetate*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, colourless needles, m. p. 109—111°; the former is soluble in dilute alkali hydroxides and in aqueous ammonia, whilst the latter dissolves sodium or potassium with the evolution of hydrogen, and is hydrolysed by aqueous-alcoholic sodium hydroxide, yielding *methanedisulphonanilinoacetic acid*, $\text{CH}_2(\text{SO}_2\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H})_2$, crystals with $2\text{H}_2\text{O}$, m. p. 110—112° (anhydrous).

Methanedisulphonphenylhydrazide, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{NHPh})_2$, colourless needles, m. p. 118—119° (decomp.), and *methanedisulphonbenzoylhydrazide*, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{NHBz})_2$, needles, m. p. 204—205° (decomp.), are prepared from methanedisulphonyl chloride and phenyl- and benzoyl-hydrazine, respectively, in ethereal or chloroform solution; the latter is soluble in aqueous alkali hydroxide.

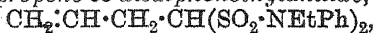
By introducing alkyl, aryl, and acyl groups in the methylene group, syntheses have been effected both with the esters and the amide derivatives of methanedisulphonic acid, but the replacement of the methylene hydrogen atoms by metals, and consequently also the course of the synthesis, depend on the nature of the

radicles attached to the SO_2 groups. The methyl and ethyl esters in ethereal or benzene solution react with the alkali metals, with the evolution of hydrogen, but the reaction becomes so slow before one atomic proportion of the metal has been added that syntheses attempted by this means follow a tedious and uncertain course; however, *ethane- α -disulphonic acid* and *propane- α -disulphonic acid* in the form of their *barium* salts have been obtained by the action of methyl and ethyl iodides, respectively, on a benzene solution of the methyl or ethyl methanedisulphonate to which potassium had been previously added. Aryl esters of methanedisulphonic acid form in aqueous solution stable salts with alkali hydroxides and with ammonia, but these salts, from some undetermined cause, are little suited for synthetic purposes in aqueous or alcoholic solution or suspension. When, however, the aryl esters are treated in an indifferent solvent with sodium, and the resulting solution or suspension is treated with alkyl haloid, methyl sulphate, or benzoyl chloride, reaction proceeds smoothly. *Phenyl ethane- α -disulphonate*, $\text{CHMe}(\text{SO}_2\text{Ph})_2$, *phenyl propane- α -disulphonate*, *phenyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 96—97°, and *phenyl butane- $\beta\beta$ -disulphonate*, an oil, have been thus prepared; also *p-tolyl ethane- α -disulphonate*, crystals, m. p. 57—60°, and *p-tolyl propane- $\beta\beta$ -disulphonate*, crystals, m. p. 88—91°, have been obtained, whilst the corresponding *o*-tolyl and *m*-tolyl esters are oily liquids.

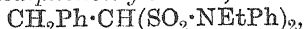
Numerous syntheses can be effected by means of the amide derivatives of methanedisulphonic acid. Any such derivative containing the NH group is inadmissible, however, because such substances form metallic derivatives containing the NNa group, and these lead to the production of *N*-substituted derivatives. The most efficient synthetic reagents are the alkylanilides,



particularly the very easily obtainable methanedisulphonethylanilide. These substances in warm benzene solution are treated with sodium or potassium, and the product is treated with an alkyl or acyl haloid. By these means, the CH_2 group of the methanedisulphonalkylanilides can be converted into CHMe , CHEt , $\text{CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, $\text{CH}\cdot\text{CH}_2\text{Ph}$, and $\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ (*p*), but alkyl haloids of greater complexity react very slowly. Further, the remaining hydrogen atom of the preceding groups can be replaced by a methyl group, giving CMe_2 , CMeEt , etc., but not by an ethyl, allyl, or other radicle. Analogously to the preceding, the sodium derivatives, $\text{CHNa}(\text{SO}_2\text{NRAr})_2$, react with the halogens, yielding derivatives containing the group CHCl , CHBr , or CHI ; from these, a dichloro-derivative, $\text{CCl}_2(\text{SO}_2\text{NRAr})_2$, can be obtained, but not a dibromo- or di-iodo-derivative. *Ethane- α -disulphonethylanilide*, $\text{CHMe}(\text{SO}_2\text{NEtPh})_2$, prisms, m. p. 150°, *ethane- α -disulphonethylphenetide*, crystals, m. p. 95—96·5°, *propane- α -disulphonethyl-anilide*, prisms, m. p. 128—129°, and the *-phenetide*, $\text{CHEt}(\text{SO}_2\text{NEt}\cdot\text{C}_6\text{H}_4\cdot\text{OEt})_2$, needles, m. p. 93·5—94·5°, Δ -*propene- $\delta\delta$ -disulphonethylanilide*,



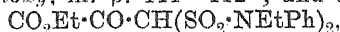
prisms, m. p. 120—121° (*dibromide*, needles, m. p. 103—106°), *β-phenylethane-αα-disulphonethylanilide*,



prisms, m. p. 104—106°, *β-p-nitrophenylethane-αα-disulphonethylanilide*, pale yellow, crystalline powder, m. p. 100—105°, *propane-ββ-disulphonethylanilide*, crystals, m. p. 130—132°, and the *-phenetidide*, m. p. 109°, *butane-ββ-disulphonethylanilide*, crystals, m. p. 114—116°, *Δ²-pentene-δδ-disulphonethylanilide*, m. p. 107° (*dibromide*, leaflets, m. p. 100—102°), and *α-phenylpropane-ββ-disulphonethylanilide*, m. p. 96·5—97°, are described.

Phenyl benzoylmethanedisulphonate, $\text{CHBz}(\text{SO}_2\text{Ph})_2$, crystals, m. p. 96°, and the corresponding *p-tolyl* ester, m. p. 91°, and *m-tolyl* ester, m. p. 102°, have been prepared.

The following acyl derivatives of methanedisulphonethylanilide are described: *formyl*, $\text{CHO}\cdot\text{CH}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 113—114°; *acetyl*, rhombic plates, m. p. 143—144°; *propionyl*, needles, m. p. 129—130°; *benzoyl*, m. p. 118—119°; *o-nitrobenzoyl*, prisms, m. p. 148—149°; *o-acetoxybenzoyl*, m. p. 152—153°; *carbethoxy*, m. p. 111—112°; and *ethoxycarbonyl*,



plates, m. p. 103—105°. *Chloromethanedisulphonethylanilide*, $\text{CHCl}(\text{SO}_2\cdot\text{NEtPh})_2$, needles, m. p. 97—98°, the *bromo-derivative*, needles, m. p. 167—168°, the *iodo-derivative*, needles, decomp. 150—170°, and *dichloro-derivative*, m. p. 109—110°, are described.

Unlike malonic acid, methanedisulphonic acid is very stable towards mineral acids, so much so that the Carius method is inapplicable to the estimation of the sulphur. The aryl esters and anilides of the dialkylated acids, $\text{C}(\text{Alk.})_2(\text{SO}_3\text{H})_2$, are resistant to acid hydrolysis, but are smoothly decomposed by alcoholic alkalis under pressure in the sense of the equations: (1) $\text{CMe}_2(\text{SO}_3\text{Ph})_2 + 5\text{NaOH} = \text{OH}\cdot\text{CMe}_2\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{Ph}\cdot\text{ONa}$ and (2) $\text{CMe}_2(\text{SO}_2\cdot\text{NEtPh})_2 + 3\text{NaOH} = \text{OH}\cdot\text{CMe}_2\cdot\text{SO}_3\text{Na} + \text{Na}_2\text{SO}_3 + 2\text{NHEtPh}$.

Sodium *β-hydroxypropane-β-sulphonate* thus obtained is not identical with the additive compound of acetone and sodium hydrogen sulphite.

Acyl derivatives of aryl esters or secondary anilides of methanedisulphonic acid are extraordinarily stable towards alkalis; the latter class of compound is decomposed by heating with mineral acids in the sense of the equation $\text{CHBz}(\text{SO}_2\cdot\text{NEtPh})_2 + 3\text{H}_2\text{O} = \text{CH}_2\text{Bz}\cdot\text{SO}_3\text{H} + \text{H}_2\text{SO}_4 + 2\text{NHEtPh}$. C. S.

Dehydration of Formic Acid Solutions. D. C. JONES (*J. Soc. Chem. Ind.*, 1919, 38, 362—363T).—It is shown that, in spite of previous statements to the contrary, phosphoric oxide can be used satisfactorily for the dehydration of concentrated solutions of formic acid. The conditions to be observed are that the calculated quantity of phosphoric oxide necessary to combine with the water present in the formic acid be added gradually, the mixture being well cooled and shaken during the addition. The formic acid is then distilled under 15—18 mm. pressure, and can

readily be obtained up to 99.5% strength. When excess of phosphoric oxide is used, considerable decomposition of the formic acid occurs.

The concentration of dilute solutions of formic acid is limited by the formation of a constant boiling mixture containing 77% of acid by weight and boiling at 107.1°. The composition of the constant boiling mixture is found to vary to a considerable degree with the pressure, decreasing in formic acid content with diminishing pressure, until at 43 mm. it contains 60.9% of formic acid, the boiling point being 38°. It is therefore possible to obtain concentrated from dilute formic acid by concentrating up to the constant boiling mixture at atmospheric pressure, and then continuing the distillation at low pressure, a separation into very concentrated formic acid and the more dilute constant boiling mixture being obtained.

E. H. R.

Preparation of Anhydrides and Chlorides of Organic Acids.

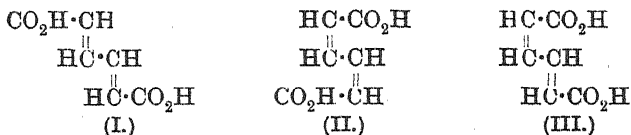
THOMAS HAROLD DURRANS and A. BOAKE, ROBERTS & Co., LTD. (Brit. Pat., 131379; addition to Brit. Pat., 128282).—Organic acid anhydrides or chlorides other than acetic anhydride or chloride may be produced by the action of chlorine on a mixture of phosphorus, preferably red phosphorus, and the alkali or alkaline earth salts of the organic acid, at temperatures preferably below 50°, and in proportions falling within those represented by the following pairs of equations for the anhydrides and chlorides respectively: $6R \cdot CO_2Na + P + 3Cl = 3(R \cdot CO)_2O + Na_3PO_3 + 3NaCl$ and $8R \cdot CO_2Na + P + 5Cl = 4(R \cdot CO)_2O + Na_3PO_4 + 5NaCl$, $3R \cdot CO_2Na + P + 3Cl = 3R \cdot COCl + Na_3PO_3$ and $4R \cdot CO_2Na + P + 5Cl = 4R \cdot COCl + Na_3PO_4$.

G. F. M.

The Action of Grignard Reagents on the Esters of certain Dicarboxylic Acids. HARRY HEPWORTH (T., 1919, 115, 1203—1210).

Oxidation of Muconic Acid. Synthesis of Mucic Acid.

ROBERT BEHREND and GEORGE HEYER (*Annalen*, 1919, 418, 294—316).—Of the three configurative formulæ possible for muconic acid, formula I is the most probable, since the only tar-



taric acid produced by oxidation with permanganate is *r*-tartaric acid; formic, carbonic, oxalic, mucic, and other unidentified acids are also formed, but the absence of *i*-tartaric acid is definitely ascertained.

Mucic acid is obtained in yields up to 36.5% of the theoretical by oxidising a neutral solution of sodium muconate with sodium chlorate in the presence of a little osmium tetroxide and a few

y*

drops of acetic acid (compare Hofmann, Ehrhart, and Schneider, A., 1913, ii, 609), *r*-idosaccharic acid being also formed in about 2% of the theoretical yield. The latter acid forms a characteristic copper salt, $C_6H_8O_8Cu \cdot 2H_2O$, microscopic prisms which become deep blue by prolonged heating at 120° , and a *phenylhydrazide*, $C_{18}H_{22}O_6N_4$, faintly yellowish-white, crystalline powder, m. p. $217-218^\circ$ (decomp.). C. S.

Reactions between Potassium Sulphate and Tartaric Acid under Various Conditions. Behaviour of Potassium Hydrogen Sulphate with Alcohol. ARTURO BORNTAEGER (*Annali Chim. Appl.*, 1919, 12, 1—23).—The readiness with which the system ($K_2SO_4 + C_4H_6O_6$) is converted into the system ($KHSO_4 + C_4H_5KO_6$) when evaporated with alcohol was shown by Bussy and Buignet (*J. Pharm. Chim.*, 1865, [v], 2, 8). When aqueous solutions containing equivalent quantities of potassium hydrogen sulphate and potassium hydrogen tartrate are evaporated, potassium sulphate and tartaric acid are first formed. On continuing the evaporation, potassium hydrogen tartrate is deposited, and this subsequently reacts with the potassium hydrogen sulphate in solution to form potassium sulphate and tartaric acid. Hence the two systems ($K_2SO_4 + C_4H_6O_6$) and ($KHSO_4 + C_4H_5KO_6$) appears to behave in an identical manner under these conditions. When the evaporation is continued to the end, a dry mixture of potassium sulphate and tartaric acid is obtained, whereas in presence of free sulphuric acid the residue would be moist. Absolutely anhydrous alcohol has no influence on potassium hydrogen sulphate, but alcohol containing a little water decomposes it slowly and partly into the normal sulphate and free sulphuric acid. On treating a dry mixture in equimolecular proportions of potassium sulphate and tartaric acid with ether or absolute alcohol, only the tartaric acid is extracted, but in presence of alcohol containing a little water, a partial reaction takes place, with the formation of potassium hydrogen tartrate and potassium hydrogen sulphate, and the latter is subsequently partly decomposed into the normal sulphate and free sulphuric acid. Similar reactions are observed when solutions of the two substances in equimolecular proportions are evaporated prior to the treatment with ether, absolute alcohol, or alcohol containing a little water. [See also *J. Soc. Chem. Ind.*, 1919, 839A.] C. A. M.

Crystallography of the Compound of Nickel Dichromate and Ethylenediamine, $NiCr_2O_7 \cdot 3C_2H_4(NH_2)_2$. GIUSEPPINA CHIAVARINO (*Riv. min. crist. Ital.*, 1917, 48, 82—85).—This salt is monoclinic; complete crystallographic data are given.

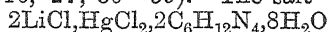
CHEMICAL ABSTRACTS.

Crystallography of the Compounds of Nickel and Magnesium Tetrathionate Octahydrates with Hexamethylenetetramine. C. PERRIER (*Riv. min. crist. Ital.*, 1916, 47, 22—30).—The salts of the formula $RS_4O_6 \cdot 2C_6H_{12}N_4 \cdot 8H_2O$,

where R=Mg or Ni, are monoclinic; complete crystallographic data are given. The isomorphism of magnesium and nickel in other compounds is discussed, and the closeness of their molecular volumes is pointed out.

CHEMICAL ABSTRACTS.

Crystallography of Compounds of Lithium Mercuric Haloids with Hexamethylenetetramine. E. QUERCIGH (*Riv. min. crist. Ital.*, 1916, 47, 30—39).—The salt



is monoclinic, the corresponding bromide triclinic, and the iodide rhombic. Full crystallographic data are given.

CHEMICAL ABSTRACTS.

The Melting Points of the Substituted Amides of the Normal Fatty Acids. PHILIP WILFRED ROBERTSON (T., 1919, 115, 1210—1223).

Action of Alkaline Solutions of Bromine on Acid Amides. HANS ODENWALD (*Annalen*, 1919, 418, 316—341).—In the method previously described (Behrend and Odenwald, this vol., i, 70) for the preparation of acetylmethylcarbamide, the yield falls from 75% to zero in the presence of an excess (15—20%) of alkali over the amount (1 mol.) required to react with the acetamide (1 mol.) and bromine (0.55 mol.). The cause of this has now been investigated. In a series of experiments, acetamide (1 mol.) was dissolved in bromine (0.5—2.0 mols.), and the solution was treated with a quantity of 18.7% potassium hydroxide solution (1.2—4.8 mols.) 20% in excess of the amount required to combine with the bromine. Carbon dioxide, ammonia, and methylamine were detected in all experiments; the amounts of these and of unchanged acetamide, in the experiments with less than 1.5 mols. of bromine, account for 0.47—0.49 mol. of acetamide. With 1.5 mols. of bromine, acetylmethylcarbamide (0.078 mol.) was detected, but not acetamide, and in the experiment with 2 mols. of bromine neither acetamide nor acetylmethylcarbamide could be detected, and the amount of carbon dioxide formed corresponded with only 0.3 mol. of acetamide. In all experiments, the balance of the acetamide was converted into products which could not be identified; the products were unsuccessfully examined for the presence of acetonitrile, methyl alcohol, hydrogen cyanide, s-dimethylcarbamide, and methylcarbamide, but very small quantities of dibromomethylamine and of nitrogen (about 0.03 mol.) were detected. The author is of opinion that the methylcarbamide in alkaline solution reacts with acetamide either not at all or very much more slowly than in acid solution; instead of forming acetylmethylcarbamide, it decomposes into carbon dioxide and methylamine, and the latter reacts more rapidly than acetamide with the hypobromite.

With the hope of obtaining less volatile products of reaction, the behaviour of an alkaline solution of bromine with *isovaleramide* has been examined. In an experiment with *isovaleramide*

(0.5 mol.), bromine (0.25 mol.), and 10% potassium hydroxide solution (0.6 mol.), the products were carbon dioxide (0.23 mol.), dibromo*isobutylamine* (0.09 mol.), ammonia and *isobutylamine* (0.02 mol.); these and unchanged *isovaleramide* (0.32 mol.) account for the whole of the amide. The reaction proceeds according to the equation $\text{C}_4\text{H}_9\cdot\text{CO}\cdot\text{NH}_2 + \text{Br}_2 + 2\text{KOH} = \text{C}_4\text{H}_9\cdot\text{NH}_2 + \text{CO}_2 + 2\text{KBr} + \text{H}_2\text{O}$, but the author has been unable to discover what is the fate of the *isobutylamine*.

It is possible that a loss of acetamide occurs in the first experiments during the evaporation of solutions. One gram of different amides has been evaporated to dryness with 20 c.c. of water, heated on the water-bath for half an hour, and again evaporated with 20 c.c. of water; the losses were, with acetamide 0.95 gram, with propionamide 0.36 gram, with *isobutyramide* 0.10 gram, and with *isovaleramide* nil.

It is quite immaterial in what order acetamide (1 mol.), *isovaleramide* (1 mol.), bromine (1 mol.), and aqueous potassium hydroxide (2 mols.) are mixed together; the products of the reaction are always the same, namely, about equal quantities (molecular) of *isovalerylisobutylcarbamide* and *acetylisobutylcarbamide*, together with a small quantity of *acetylmethylcarbamide*; it is remarkable that the fourth possible product, *isovalerylmethylcarbamide*, could not be detected. Analogous results are obtained with acetamide and propionamide, and with acetamide and *isobutyramide*.

Acetylisobutylcarbamide, $\text{C}_7\text{H}_{14}\text{O}_2\text{N}_2$, forms long, six-sided leaflets, m. p. 109—114°, and *acetylisopropylcarbamide*, hexagonal crystals, m. p. 68—72°, which become superficially oily after long keeping. C. S.

The Constitution of Carbamides. X. The Behaviour of Urea and of Thiourea towards Diazomethane and Diazoethane respectively. The Oxidation of Thiourea by Potassium Permanganate. EMIL ALPHONSE WERNER (T., 1919, 115, 1168—1174).

Some Cases of Solubility Influence. I. Compounds of Thiosinamine [Allylthiocarbamide] Existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 175—191).—Cryoscopic investigation of solutions containing thiocarbamide or allylthiocarbamide, together with either sodium salicylate or resorcinol or antipyrine, leads to anomalous results which are explainable on the assumption that compounds between the different pairs of solutes are formed in solution. None of these compounds has been separated in the solid condition. T. H. P.

The Rotatory Powers of the Amides of Several α -Hydroxyacids of the Sugar Group. C. S. HUDSON and SHIGERU KOMATSU (*J. Amer. Chem. Soc.*, 1919, 41, 1141—1147).—The generalisations announced in an earlier paper, based largely on Weerman's work (A., 1918, i, 292), have been amplified and extended by further

and more trustworthy data. The material examined makes it possible to calculate the molecular rotation due to each active carbon atom in a number of series by the method already employed in the case of certain phenylhydrazides (A., 1917, i, 318). The following table gives the values as far as it is possible to determine them, the sign of the rotation being for the isomeride which has the hydroxyl group attached to the particular carbon atom placed to the right of the formula, written vertically, with the amide group at the top.

Carbon.	4-C series diamide.	Pentonic amides.	Hexonic amides.	Heptonic amides.	Hexaric diamides.
α	+7880	+4450	+4725	+4585	+3925
β	—	-2315	-1465	-1960	-1385
γ	—	+575	+95	?	—
δ	—	—	-205	-420	—

The values for the β - and γ -carbon atoms in the series of pentonic amides are probably untrustworthy, as they depend on a value of the rotation of *d*-xylonamide which is doubtful.

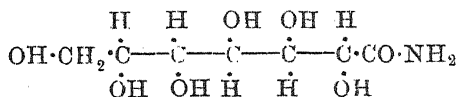
It is interesting to note how the sign of the rotation alternates from carbon to carbon, and how much the rotation of the whole molecule depends on the configuration about the α - and β -carbon atoms. The table also illustrates the principle of optical superposition in the sugar group.

The amides prepared by the authors themselves, usually by the action of ammonia on the lactones, are as follows, the values of $[\alpha]_D^{20}$ being for aqueous solutions: *d*-galactonamide, m. p. 172—172.5°, $[\alpha]_D^{20} + 30.2^\circ$; *d*-gluconamide, m. p. 143—144°, $[\alpha]_D^{20} + 31.2^\circ$; *d*-gulonamide, m. p. 122—123°, $[\alpha]_D^{20} + 15.2^\circ$; *d*-mannonamide, m. p. 172—173°, $[\alpha]_D^{20} - 17.3^\circ$; α -*d*-glucoheptonamide, m. p. 134.5°, $[\alpha]_D^{20} + 10.6^\circ$; β -*d*-glucoheptonamide, m. p. 158°, $[\alpha]_D^{20} - 30.2^\circ$; α -*d*-galaheptonamide, m. p. 206°, $[\alpha]_D^{20} + 14.3^\circ$; *l*-arabonamide, m. p. 135—136°, $[\alpha]_D^{20} + 37.5^\circ$; *l*-ribonamide, m. p. 137—138°, $[\alpha]_D^{20} - 16.4^\circ$; *d*-mannosaccharodiamide, m. p. 188—189.5° (decomp.), $[\alpha]_D^{20} - 24.5^\circ$; *d*-saccharodiamide, m. p. 172—173°, $[\alpha]_D^{20} + 13.3^\circ$.
J. C. W.

The Amide of α -*d*-Mannoheptonic Acid. C. S. HUDSON and K. P. MONROE (*J. Amer. Chem. Soc.*, 1919, **41**, 1140—1141).—This amide was first obtained by Fischer by the action of hydrogen cyanide on *d*-mannose, but it is not easy to purify it if made in this way. A better method is the action of ammonia on a solution of α -*d*-mannoheptonolactone in 50% alcohol.

α -*d*-Mannoheptonamide (annexed formula) has m. p. 193—194° and $[\alpha]_D^{20} + 28.0^\circ$, the molecular rotation being almost the same as that of *d*-galactonamide and *l*-arabonamide, in which the configuration of the molecule with regard to the α -, β -, and γ -carbon atoms is the same.

J. C. W.



Preparation of Cyanogen Chloride. W. L. JENNINGS and W. B. SCOTT (*J. Amer. Chem. Soc.*, 1919, **41**, 1241—1248).—The authors review the history of cyanogen chloride, and report that the most suitable reaction for its preparation is that of chlorine on an alkali cyanide. Water is necessary in this reaction, but its amount must be restricted, otherwise too much heat is developed and some of the product is polymerised. The best procedure is as follows. Finely powdered sodium cyanide is mixed with 2% of its weight of water and just sufficient carbon tetrachloride to prevent the mass from becoming pasty. The mixture is cooled to -5° and submitted to the action of a current of well-washed chlorine, so regulated that the temperature is maintained at about -3° . The flask is connected with a calcium chloride tube and then a U-tube immersed in a freezing mixture, and when absorption is complete, as indicated by a bubbler at the final exit, the temperature is allowed to rise to 10° , and finally to 28° , so as to distil the cyanogen chloride. The crude product is usually of a yellow colour through dissolved chlorine, but this is removed by freezing or by leaving the liquid over mercury in a sealed tube. The yield is almost quantitative, and there are no risks of explosion.

Pure cyanogen chloride is a colourless liquid, b. p. $13^{\circ}/748$ mm., m. p. -5° to -6° , and does not polymerise. The presence of traces of hydrogen chloride, however, induces polymerisation, and if suspected should be counteracted by treatment with lime.

J. C. W.

Preparation of Cyanogen Chloride by Held's Method. CH. MAUGUIN and L. J. SIMON (*Compt. rend.*, 1919, **169**, 383—386).—Held's method for preparing cyanogen chloride from potassium cyanide and chlorine (*A.*, 1898, i, 547) gives good results only if the proportion of zinc sulphate added is that required by the equation $4\text{KCN} + \text{ZnSO}_4 = \text{Zn}(\text{CN})_2 + 2\text{KCN} + \text{K}_2\text{SO}_4$, a yield of 80% being then obtained. Methods for controlling the purity of the product are described.

T. H. P.

Compounds of Univalent Nickel. II. I. BELLUCCI (*Gazzetta*, 1919, **49**, ii, 70—81. Compare *A.*, 1914, i, 260; also Tschugaev and Chlopin, *A.*, 1914, ii, 660).—The aqueous solution of red potassium nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_3$, prepared by gradual addition of alkali metal amalgam to the aqueous solution of the yellow nickelocyanide, $\text{K}_2\text{Ni}(\text{CN})_4$, in an atmosphere of hydrogen, readily assumes the original yellow colour, oxidation being effected either by atmospheric oxygen, or by aqueous oxygen with liberation of the hydrogen, or by an oxidising agent such as hydrogen peroxide. The red solution may be preserved from appreciable oxidation for some days by employing boiled water in its preparation and by adding concentrated potassium hydroxide solution to the liquid and covering the latter with a layer of light petroleum.

Oxidation of the red nickelocyanide by means of hydrogen peroxide in absence of alkali cyanide takes place according to the

equation, $4\text{K}_2\text{Ni}(\text{CN})_3 + 2\text{H}_2\text{O}_2 = 3\text{K}_2\text{Ni}(\text{CN})_4 + \text{Ni}(\text{OH})_2 + 2\text{KOH}$. Further, when an aqueous solution of the pure, red nickelocyanide is boiled for some time in a reflux apparatus in a stream of hydrogen, metallic nickel is precipitated, and the yellow nickelocyanide remains in the solution, the proportions of the total nickel in precipitate and solution being very nearly 1:3 (actually 1:3.16): $4\text{K}_2\text{Ni}(\text{CN})_3 + 2\text{H}_2\text{O} = 3\text{K}_2\text{Ni}(\text{CN})_4 + \text{Ni} + 2\text{KOH} + \text{H}_2$; the same reaction occurs, only far more slowly, at the ordinary temperature. Such separation of metallic nickel from a compound of univalent nickel may be represented by the scheme, $2\text{Ni}' \rightarrow \text{Ni}'' + \text{Ni}$, and is analogous to the separation of copper from a cuprous salt with formation of a cupric salt, $2\text{Cu}' \rightarrow \text{Cu}'' + \text{Cu}$.

T. H. P.

Production of Aromatic Nitro-compounds. FERDINAND GROS & BOUCHARDY and LUCIEN JEAN JOSEPH PERRUCHE (Brit. Pat., 131982).—Aromatic nitro-compounds are prepared by passing oxygen, air, or ozonised air, preferably under pressure, into a mixture of the substance to be nitrated with liquid nitrogen peroxide and traces of water, the temperature being maintained at $0-20^\circ$. Nitric acid is first produced according to the equation $\text{N}_2\text{O}_4 + \text{H}_2\text{O} + \text{O} = 2\text{HNO}_3$, and instantly reacts with the aromatic compound, regenerating water, and the cycle of operations is repeated until the reaction mixture contains only the nitro-compound, nitric acid, and the excess of nitrogen peroxide used; the last is recovered by distillation or by a current of hot air. The nitro-compound may then be isolated after neutralising the nitric acid, or it may be further nitrated by treating the residual mixture with sulphuric acid. If necessary, the violence of the nitration may be moderated by adding to the reaction mixture an inert diluent, such as carbon tetrachloride, before admitting the oxygen.

G. F. M.

Preparation of *N*-Monoalkyl Derivatives of certain Aromatic Compounds. ARTHUR LAPWORTH and LEVINSTEIN, LTD. (Eng. Pat., 132555).—Benzylidene derivatives of *p*-substituted monoamines or of other monoamines of the benzene and naphthalene series substituted by indifferent groups in the nucleus, which either as amines or as alkylamines do not react with benzaldehyde in the presence of acids to form amino-derivatives of triarylmethanes, are treated in the absence of alkali with alkyl sulphates or alkyl esters of benzenesulphonic acid. The products are hydrolysed and the *N*-monoalkylarylamines are separated from the mixture. Examples of the process are described in relation to the benzylidene derivatives of *p*-aminophenol, *p*-toluidine, and 1-bromo-2-naphthylamine. The benzylidene compound is dissolved in boiling benzene, the pure alkylating agent, such as methyl sulphate, is added, and the mixture boiled for some hours. The product is hydrolysed by the addition of hydrochloric acid and a little water, the benzaldehyde and benzene are removed by distillation with steam, the *N*-alkylated base is liberated from the residue and

separated from the other products in any suitable manner, for example, by conversion into the nitroso-compound. J. F. B.

Preparation of Diphenylamine. HOMER ROGERS and E. J. DU PONT DE NEMOURS & Co. (U.S. Pat. 1314538).—The condensation of aniline to diphenylamine is effected by heating the aniline in the presence of water and a catalyst consisting of a substance containing bromine. J. F. B.

β -Naphthylmethylaniline. GILBERT T. MORGAN and FREDERICK PAGE EVANS (T., 1919, 115, 1140—1145).

The Oxidation of Phenol Derivatives. CYRIL NORMAN HINSHELWOOD (T., 1919, 115, 1180—1188).

Oxidation of Phenols by Gaseous Oxygen and the Catalytic Effect of Metals. F. W. SKIRROW (*Canadian Chem. J.*, 1919, 3, 292—294).—The oxidation which takes place when *o*-cresol or a solution of cresol in benzene is brought into contact with air or oxygen in the presence of copper was measured by connecting the tube containing the reacting substances with a mercury manometer and recording the rate of absorption by the fall in pressure. It was found that there was an initial period during which there was little, if any, absorption. In a blank experiment in which the air in the tube was replaced by nitrogen, no absorption occurred, and the cresol in the tube did not darken even after three years' exposure to light. In another series of experiments, the flask containing the benzene solution of cresol and the copper was connected with a gas burette containing oxygen saturated with benzene over mercury, and the decrease in the volume was measured in the usual way. Here, too, the initial delay in the absorption was noticed, and this was attributed either to the presence of a substance retarding the oxidation or to the necessity of the formation of a catalytic compound. In support of the former view was the fact that the oxidation proceeded more consistently when the oxygen derived from potassium chlorate was replaced by electrolytic oxygen freed from all traces of ozone. Green crystals containing 44.9% of copper (after drying at 100°) were present in the dark liquid after the oxidation. As this amount of copper does not correspond with the composition of any of the probable compounds, it is possible that the benzene ring is broken during the absorption. A similar oxidation was observed in the case of phenol, but more slowly than with *o*-cresol, and here too the initial stage of very slow absorption was present. [See also *J. Soc. Chem. Ind.*, 1919, 812A.] C. A. M.

Chloropicrin. I. JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX (T., 1919, 115, 1188—1194).

Crystallography of Ammonium Picrate and of Potassium Trithionate. HERBERT E. MERWIN (*J. Washington Acad. Sci.*, 1919, 9, 429—431).—The orthorhombic crystals of ammonium

picrate are tabular, acicular, or granular in habit. Optical constants are given; refractive indices (Na) $\alpha=1.508$, $\beta=1.872$, $\gamma=1.908$. There is a change in the optic axial plane for different colours, and at wave-length $541\mu\mu$ the crystals are optically uniaxial. Blades of potassium trithionate crystallised from a hot saturated solution show a slight variation in the angles of the prism. Optical constants are given; refractive indices (Na) $\alpha=1.4934$, $\beta=1.5641$, $\gamma=1.602$.
L. J. S.

Mercury Mercaptide Nitrites and their Reaction with the Alkyl Iodides. VII. Chain Compounds of Sulphur (*continued*).
SIR PRAFULLA CHANDRA RÂY and PRAFULLA CHANDRA GUHA (T., 1919, 115, 1148—1155).

The Electrolytic Reduction of Phenylacetic Acid. C. MARIE, R. MARQUIS, and BIRCKENSTOCK (*Bull. Soc. chim.*, 1919, [iv], 25, 512—516).—Phenylacetic acid can be reduced by electrolytic methods in a sulphuric acid solution, using a lead cathode. The yield is small, owing to a portion of the phenylethyl alcohol formed combining with the sulphuric acid and being subsequently oxidised at the anode. The only portion of the alcohol which escapes this destruction is that which, at the moment of its formation, combines with the excess of phenylacetic acid present.
W. G.

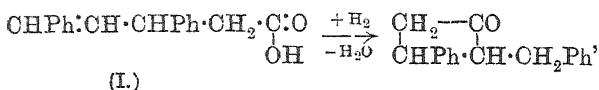
Syntheses of Naphthyl-lactic and Naphthylcinnamic Acids.
I. β -Phenyl- β - α -naphthyl-lactic Acid and β - α -Naphthylcinnamic Acid. REMO DE FAZI (*Gazzetta*, 1919, 49, i, 242—251).— *β -Phenyl- β - α -naphthyl-lactic acid*, $C_{10}H_7\cdot CPh(OH)\cdot CH_2\cdot CO_2H$, obtained as ethyl ester by decomposing by means of acidified water, the complex, $C_{10}H_7\cdot CPh(O\cdot ZnBr)\cdot CH_2\cdot CO_2Et$, formed by the interaction of phenyl α -naphthyl ketone and ethyl bromoacetate in presence of zinc dust, crystallises in slender, colourless, silky needles of peculiar odour, m. p. 188—189°, and with concentrated sulphuric acid in the cold gives a transitory, green coloration changing to reddish-brown. Its *ethyl* ester forms tufts of slender, white needles, m. p. 95—96°, and gives the same colorations with sulphuric acid as the free acid.

β - α -Naphthylcinnamic acid, $C_{10}H_7\cdot CPh:CH\cdot CO_2H$, obtained as ethyl ester by dehydrating ethyl β -phenyl- β - α -naphthyl-lactate in benzene solution by means of phosphoric oxide, forms silky, white needles, m. p. 219—220°. With concentrated sulphuric acid it first gives a transitory, emerald-green coloration, and then dissolves to a reddish-brown solution with a green fluorescence; on addition of water, the acid solution becomes yellow and yields a precipitate, which is probably the corresponding indone. The *ethyl* ester forms a pale yellow oil, b. p. 278—281°/2 mm., or shining needles, m. p. 69—71° (?), and with concentrated sulphuric acid gives a transitory, green coloration, rapidly changing to reddish-brown.

T. H. P.

Asymmetric Replacement in the meta-Series. I. WILLIAM HENRY GOUGH and JOCELYN FIELD THORPE (T., 1919, 115, 1155—1164).

Some Factors bearing on 1:6-Addition. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1919, **41**, 1132—1140).—In all the cases in which addition in the 1:6-position has been observed, the unsaturated compound has also had an ethylenic linking in the 3:4-position (compare Straus, A., 1910, i, 119). The author has now synthesised the compound (I) without this disturbing element, but finds that it is abnormal in behaviour. When reduced, for example, it was expected to yield a ketone, thus:



but it could not be reduced either by zinc and acetic acid or sodium amalgam.

Phenyl styryl ketone is condensed with methyl or ethyl malonate (Kohler, A., 1911, i, 984), the esters are hydrolysed, and the ketonic acid is reduced by means of sodium amalgam. Two by-products of the reduction are mentioned, namely, *βδ*-diphenylvalerolactone, $\text{O} < \underset{\text{CO---CH}_2}{\text{CHPh}\cdot\text{CH}_2} > \text{CHPh}$, needles, m. p. 113—114°, and *δ*-hydroxy-*βδ*-diphenylbutane-*αα*-dicarboxylic acid,

$\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}(\text{CO}_2\text{H})_2\cdot 2\text{H}_2\text{O}$, nodules of stout needles, m. p. 190—195° (decomp.), but the chief product is *δ*-hydroxy-*βδ*-diphenylvaleric acid, which crystallises with $0\cdot5\text{H}_2\text{O}$, in needles from benzene or pearly flakes from alcohol, m. p. 154—154·5°. When boiled with acetic anhydride and a little sulphuric acid, this compound changes into the desired unsaturated acid, accompanied in one experiment by an *internal* ester, $\text{O} < \underset{\text{CO}\cdot\text{CH}_2}{\text{CHPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}} > \text{O}$, m. p. 92—94°.

βδ-Diphenyl-*Δ*-butene-*α*-carboxylic acid (I) crystallises from benzene in colourless, rhombic needles, m. p. 124—125°, and forms a *methyl* ester, clusters of stout needles, m. p. 47—48°, which reacts with magnesium phenyl bromide to form the *carbinol*, $\text{CHPh}:\text{CH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{OH}$, in thin needles, m. p. 138—139°.

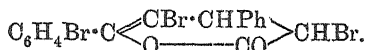
J. C. W.

The cycloPropane Series. V. E. P. KOHLER and L. L. STEELE (*J. Amer. Chem. Soc.*, 1919, **41**, 1093—1105. Compare A., 1917, i, 566—570; 1918, i, 72; this vol., i, 404).—All the cyclopropane derivatives described in the earlier papers have had two carboxyl groups (or ester groups) attached to one of the ring carbon atoms. The authors have now attempted to prepare monocarboxylic acids of this series, but have encountered great difficulties before achieving a measure of success.

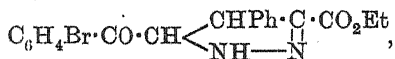
In the first place, benzoylphenylcyclopropanedicarboxylic acid loses carbon dioxide on heating, but the yield of the monocarboxylic acid is insignificant, no matter what modifications of the treatment are tried (compare A., 1917, i, 566).

A second scheme is based on the elimination of hydrogen bromide

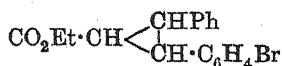
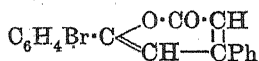
from an α -bromo-ketonic ester. γ -p-Bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, needles, m. p. 152—153°, is prepared by heating the corresponding malonic acid (A., 1918, i, 72), converted into the methyl ester, stout needles, m. p. 93°, and this is brominated. Methyl γ -bromo- γ -p-bromobenzoyl- β -phenylbutyrate is obtained in two forms, chiefly slender needles, m. p. 81—82°, but also long, feathery crystals, m. p. 92°. When it is heated with potassium acetate in methyl alcohol, the product is not a cyclopropane derivative, but γ -p-bromobenzoyl- β -phenylbutyrolactone, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{O} \\ \diagup \end{smallmatrix}\text{CO} \\ \diagdown \text{CHPh}\cdot\text{CH}_2$, colourless needles, m. p. 158°. The same lactone may be obtained by the action of sodium carbonate on γ -bromo- γ -p-bromobenzoyl- β -phenylbutyric acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, m. p. 146—147°, this being formed by the bromination of the above free butyric acid derivative. In addition, when this γ -bromo-acid is warmed with phosphorus tribromide and bromine, it yields a compound which crystallises in large, rhombic crystals, like smoky quartz, and is probably represented by the formula



The successful scheme is an adaptation of Buchner's method for preparing cyclopropane acids from pyrazolines. $\alpha\beta$ -Unsaturated ketones are condensed with ethyl diazoacetate to give ketonic pyrazolines, and these are heated. The chief product is a pyrone, but a yield of about 40% of a cyclopropane derivative may be obtained if the decomposition is carried out in the presence of platinum scrap. In the preliminary trials of this scheme, p-bromophenyl styryl ketone was used. When heated with ethyl diazoacetate at 95—175°, this yields an ester which may be hydrolysed to 5-p-bromobenzoyl-4-phenylpyrazole-3-carboxylic acid, $\text{C}_6\text{H}_4\text{Br}\cdot\text{CO}\cdot\text{C}\begin{smallmatrix} \diagup \text{CPh}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ \diagdown \text{NH}-\text{N} \end{smallmatrix}$, feathery needles, m. p. 216—217° (decomp.), which changes at 245° into 5-p-bromobenzoyl-4-phenylpyrazole, m. p. 159°. If the reaction mixture is diluted with light petroleum, however, the product is the desired ethyl 5-p-bromobenzoyl-4-phenylpyrazoline-3-carboxylate,



rhombic plates, m. p. 150—154° (decomp.). This loses nitrogen at 170—200°, changing into a mixture of 6-p-bromophenyl-4-phenyl-1:2-pyrone, feathery crystals, m. p. 183°, and a trace of ethyl 3-p-bromophenyl-2-phenylcyclopropane-1-carboxylate, needles, m. p. 118—119°.

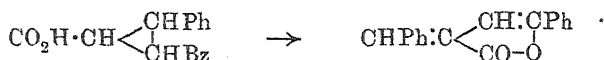


In the main experiments, unsubstituted phenyl styryl ketone was

used. This reacts with ethyl diazoacetate as above to form *ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate*. This crystallises in hexagonal plates, m. p. 156—158°, which change when kept for some time just below the decomposition temperature into an *isomeride*, needles, m. p. 102·5—103°. Both forms, in alcoholic solution, give a vivid red colour with a trace of hydrogen chloride. When heated alone at a high temperature, the product consists almost entirely of 4:6-diphenyl-1:2-pyrone, yellow plates, m. p. 138—139°, but in the presence of platinum, at 220—225°, a 37% yield of *ethyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate* is obtained. This crystallises in thin plates, m. p. 103°, is stable at 300°, and does not reduce an acetone solution of permanganate.

The free acid, $\text{CO}_2\text{H}\cdot\text{CH} \begin{smallmatrix} \text{CHPh} \\ \text{CHBz} \end{smallmatrix}$, as obtained by hydrolysis with aqueous-alcoholic potassium hydroxide in the cold, exists in two stereoisomeric forms, slender needles, m. p. 176°, and long threads, m. p. 147—150°, the latter being the more soluble in benzene, and yielding an isomeric *ethyl ester*, m. p. 93—94°, when its silver salt is treated with ethyl iodide.

It is interesting to compare the new acid and ester with Buchner's 2-phenylcyclopropane-1:3-dicarboxylic acid and the 3-benzoyl-2-phenylcyclopropane-1:1-dicarboxylic acid of the earlier papers. The new acid is decomposed when heated with hydrobromic acid in a sealed tube, whereas Buchner's acid is quite stable. When left with hydrogen bromide dissolved in acetic acid, however, it suffers rupture of the ring between carbon atoms 2 and 3, like the 1:1-dicarboxylic acid, only more readily, the product being γ -phenyl- α -benzylidenecrotonolactone, thus:

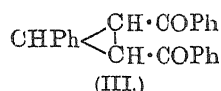
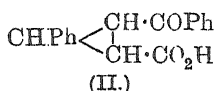
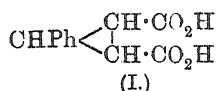


(see A., 1917, i, 566). Hydrochloric acid under the same conditions gives an unstable acid, $\text{CHPhCl}\cdot\text{CH}(\text{CO}_2\text{H})\cdot\text{CH}_2\text{Bz}$, m. p. 131—132°, which changes above its m. p. into β -benzylidenepropiophenone, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Bz}$. The corresponding ester, *ethyl β -chloro- α -phenacyl- β -phenylpropionate*, hexagonal plates, m. p. 68—69°, is stable, and may be obtained most readily by the action of alcoholic hydrogen chloride on the cyclic acid or its ester. The cyclic ester also behaves as an unsaturated compound towards zinc and acetic acid, being reduced to the ester of γ -benzoyl- β -phenylpropionic acid. A great difference between methyl 3-benzoyl-2-phenylcyclopropane-1-carboxylate and the 1:1-dicarboxylates, however, lies in their behaviour towards basic agents. The latter are most easily ruptured between the carbon atoms 1 and 3, but the new ester is indifferent to dry alkyl oxides, and no means of effecting the same opening of the ring have been found.

ω -Nitrostyrene also reacts very vigorously with ethyl diazoacetate, but the primary nitropyrzoline loses nitrous acid so readily that it changes spontaneously into *ethyl 4-phenylpyrazole-3-carboxylate*, plates, m. p. 164—165°. The corresponding acid,

$\text{CO}_2\text{H}\cdot\text{C} \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{N} \text{---} \text{NH} \end{smallmatrix}$ m. p. 252—253°, changes into 4-phenylpyrazole when heated above 250°. J. C. W.

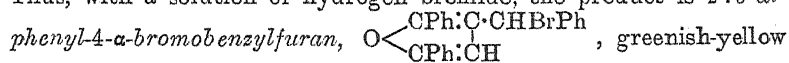
The cycloPropane Series. VI. E. P. KOHLER and W. N. JONES (*J. Amer. Chem. Soc.*, 1919, **41**, 1249—1263).—In the last paper (preceding abstract) a comparison was made between the properties of the cyclopropanedicarboxylic acid (I) and the ketonic acid (II). The diketone (III) has now been synthesised and studied in the same manner.



Benzylidenediacetophenone (Kostanecki, A., 1896, i, 556) reacts with bromine in slightly warmed chloroform to give two products, according to the proportion of bromine, namely, β -bromo- α -*tri*-phenylpentane- α -dione, $\text{COPh}\cdot\text{CHBr}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{COPh}$, m. p. 131° (decomp.), and $\beta\delta$ -dibromo- α -*tri*-phenylpentane- α -dione, m. p. 149° (decomp.). Both substances may be converted into 1:2-dibenzoyl-3-phenylcyclopropane, the former by treatment with sodium ethoxide solution, giving a modification which crystallises in needles, m. p. 116°, the latter by boiling with alcoholic potassium iodide, giving an isomeride which has m. p. 151°, but changes into the form with m. p. 116° on crystallisation from alcohol containing 1% of sodium hydroxide. Both forms of the diketone yield the same *monoxime*, m. p. 144°, and *dioxime*, needles, m. p. 175°.

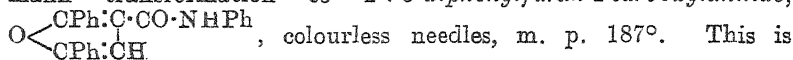
The diketone is remarkably sensitive to reducing agents. When boiled with moist alcohol and zinc dust, it forms the parent benzylidenediacetophenone, the ring being opened at the point where it was originally closed.

Unlike the ketonic acid (II), the diketone does not react with alcoholic solutions of hydrogen chloride or bromide. With glacial acetic acid solutions, however, it behaves like other cyclopropane derivatives described in this series of papers, the ring being opened between the carbon atoms 2 and 3. The resulting 1:4-diketone then loses water and changes, as usual, into a furan derivative. Thus, with a solution of hydrogen bromide, the product is 2:5-di-



prisms, m. p. 110°. This is capable of yielding a number of reactive substances, through which it may ultimately be converted into 2:5-diphenylfuran, and thus identified. With potassium acetate and acetic acid, for example, it forms 2:5-di-phenyl-4- α -acetoxybenzylfuran, yellow needles, m. p. 84°, which may be hydrolysed by alcoholic hydrochloric acid to 2:5-di-phenyl-4- α -hydroxybenzylfuran. This may also be obtained by the action of sodium methoxide solution on the bromobenzyl compound. It

crystallises in needles, m. p. 105° , and may be oxidised by chromic acid in cold acetic acid solution to a *product*, $C_{23}H_{18}O_3 \cdot H_2O$, m. p. 89° , which readily loses H_2O at 110° , or $2H_2O$ when boiled with alcoholic potassium hydroxide, methyl-alcoholic hydrogen chloride, or acetic anhydride and sodium acetate, giving *4-benzoyl-2:5-diphenylfuran*, which crystallises in yellow needles, and forms a *3-bromo-compound*, m. p. 120° , when treated with bromine in chloroform. The *oxime* of the benzoyl derivative crystallises in rosettes of needles, m. p. 174° , and readily undergoes the Beckmann transformation to *2:5-diphenylfuran-4-carboxylanilide*,



This is hydrolysed by alcoholic potassium hydroxide to the known *2:5-diphenylfuran-4-carboxylic acid*, m. p. 217° , which changes into *2:5-diphenylfuran* when distilled with zinc dust.

The cyclic diketone reacts with Grignard agents without rupture of the ring, giving ditertiary alcohols. *3-Phenyl-1:2-di-diphenyl-carbinolcyclopropane*, $\text{CHPh} \begin{array}{l} \text{CH} \cdot \text{CPh}_2 \cdot \text{OH} \\ \text{CH} \cdot \text{CPh}_2 \cdot \text{OH} \end{array}$, crystallises in clusters of slender needles, m. p. 183° , and *3-phenyl-1:2-di- α -phenyl- α -ethyl-carbinolcyclopropane* has m. p. 129° .

The diketone reacts with phosphorus pentachloride in boiling benzene to form *$\alpha\delta$ -dichloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^{α} -butene*, $\text{CHPhCl} \cdot \text{CHBz} \cdot \text{CH} \cdot \text{CPhCl}$, m. p. 122° , which is transformed into *α -chloro- γ -benzoyl- $\alpha\delta$ -diphenyl- Δ^{α} -butadiene*, prisms, m. p. 84° , when boiled with methyl-alcoholic potassium acetate. The latter compound reacts with magnesium phenyl chloride to give *α -chloro- γ -benzoyl- $\alpha\delta\delta$ -triphenyl- Δ^{α} -butene*, $\text{CHPh}_2 \cdot \text{CHBz} \cdot \text{CH} \cdot \text{CPhCl}$, in large, colourless prisms, m. p. 140° .

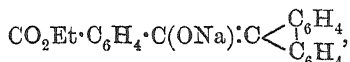
The action of bromine in warm chloroform on the cyclic diketone is somewhat obscure, but the *product*, $C_{23}H_{18}O_2Br_2$, m. p. 129° (decomp.), is isomeric with the dibromide obtained in the first instance from benzylidenediacetophenone, since it yields the same compounds when treated with potassium iodide or alcoholic potassium acetate. In the latter reaction, the product is either *2-bromo-1:2-dibenzoyl-3-phenylcyclopropane*, needles, m. p. 122° , or *2-acetoxy-1:2-dibenzoyl-3-phenylcyclopropane*, m. p. 159° , according to the proportion of potassium acetate employed. The latter could not be hydrolysed to the hydroxy-derivative. Alkaline agents give oily residues, whilst treatment with alcoholic hydrogen chloride results in the formation of *2-benzoyl-3:5-diphenylfuran*, which crystallises in plates, m. p. 118° , forms a *4-bromo-derivative*, m. p. 110° , and may be reduced by means of zinc and acetic acid to *3:5-diphenyl-2-benzylfuran*, bright yellow needles, m. p. 193° . The *oxime* of the benzoyl compound, m. p. 152° , suffers the Beckmann transformation to *3:5-diphenylfuran-2-carboxylanilide*, $\text{CH} \cdot \text{CPh} \cdot \text{O}$

$\text{CHPh} = \text{C} \cdot \text{CO} \cdot \text{NHPh}$, m. p. 143° , and this may be hydrolysed to *3:5-diphenylfuran-2-carboxylic acid*, m. p. 194°

(decomp.). This acid yields the known 3:5-diphenylfuran when distilled with zinc dust (Engler and Dengler, A., 1893, i, 512).

J. C. W.

Condensation of Ethyl Phthalate with Fluorene. WILHELM WISLICIENUS and PETER NEBER (*Annalen*, 1919, 418, 274—293).—A mixture of fluorene (1 mol.), sodium (1 atom), and ethyl phthalate (about 1.14 mols.) is heated on the water-bath until the sodium has disappeared, and is then treated, after cooling, with benzene and ice, whereby the *sodium* derivative of ethyl fluorene-phthaloylate (*o*-carbethoxyphenyl fluorenyl ketone),

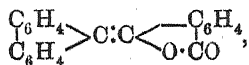


yellowish-white needles with $5\text{H}_2\text{O}$, is obtained, which is remarkably stable to boiling dilute alkali hydroxide solution. In aqueous solution it is decomposed by carbon dioxide or dilute hydrochloric acid, yielding the α -modification, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})\cdot\text{C}\begin{array}{l} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array}$, of

o-carbethoxyphenyl fluorenyl ketone, microscopic prisms, m. p. 217—218°; lower m. p.'s, dependent on the method of crystallisation, are frequently obtained in consequence of partial conversion into the β -modification. The α -modification does not react with ferric chloride, but it decolorises bromine in alcoholic solution and forms a *copper* derivative, $(\text{C}_{23}\text{H}_{17}\text{O}_3)_2\text{Cu}\cdot\text{H}_2\text{O}$, bluish-green needles, m. p. about 180°; by bromination in chloroform in the presence of a little phosphorus pentabromide, it yields *o*-carbethoxyphenyl 9-bromofluorenyl ketone, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CBr}\begin{array}{l} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array}$, colourless prisms, m. p. 190—191°.

By keeping for several weeks, the α -modification changes into the stable β -modification, $\text{CO}_2\text{Et}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\begin{array}{l} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{array}$, colourless leaflets or prisms, m. p. 140—141°. The change is effected more rapidly by distillation in a vacuum, by heating at 220°, or, most simply, by boiling with alcohol. The conversion of the β - into the α -modification is effected, through the sodium derivative, by means of alcoholic sodium hydroxide solution. The β -modification does not form a copper derivative and does not react with bromine in alcoholic solution. Both modifications are remarkably stable to alkalis; they are only decomposed by an excess of alcoholic alkali at 150°, yielding ethyl alcohol, alkali phthalate, and fluorene.

By heating above 220°, by distillation in a vacuum or, best, by heating with potassium hydrogen sulphate at 230°, either modification is converted into *phthalylfluorene*, yellow, flattened needles, m. p. 204—206°. To this substance is ascribed, not the indanedi-one formula, but the asymmetric constitution,

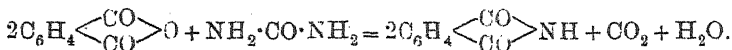


in order to account for its intense yellow colour, its easy decomposition by alkalis into *fluorenephthaloylic acid* (*o*-carboxyphenyl *fluorenyl ketone*), $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\text{C}_6\text{H}_4$, colourless crystals, m. p. 188—189° (yellow *dipotassium salt*, $\text{C}_{21}\text{H}_{12}\text{O}_3\text{K}_2$), and its conversion in boiling alcoholic solution by an excess of hydrazine hydrate into fluorene and phthalylhydrazide. It can also be prepared by heating a mixture of phthalic anhydride, fluorene, and anhydrous potassium acetate at 200—220°.

The *hydrazide*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}<\text{C}_6\text{H}_4$, glassy plates, prepared by shaking a suspension of phthalylfluorene in alcohol with hydrazine hydrate, does not melt below 200° when examined in the usual manner, but melts with decomposition (loss of water) when placed in a bath heated at 190°, and then resolidifies. When heated for half an hour at 220°, it is converted into 1-*fluorenyl-phthalazone*, $\text{C}_6\text{H}_4>\text{CH}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \text{C}_6\text{H}_4 \end{smallmatrix}\text{N}=\text{NH}$, leaflets, m. p. 275—277°.

Phthalylfluorene is reduced to *o*-*fluorenylmethylbenzoic acid*, $\text{C}_6\text{H}_4>\text{CH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, groups of faintly yellow needles, m. p. 185—186°, by heating with fuming hydriodic acid and amorphous phosphorus at 160° for eight hours. C. S.

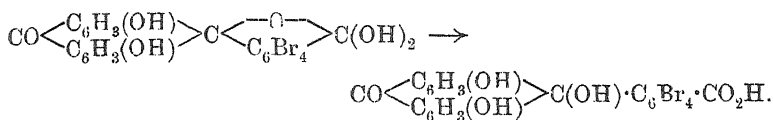
Method for the Preparation of Phthalimide. WALTER HERZOG (*Zeitsch. angew. Chem.*, 1919, **32**, 301).—Phthalic anhydride (2 mols.) and carbamide (1 mol.) are heated together in a long-necked flask; reaction commences at 130° to 135°, and the temperature rises to 150° without further external heating. At the end of the reaction, the liquid mass solidifies suddenly. When cold, the porous solid is washed with a small quantity of water and dried; it consists of practically pure phthalimide m. p. 230—231°, the yield being 90% or more of the amount required by the equation



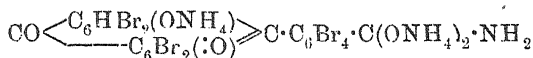
A similar reaction takes place between thiocarbamide and phthalic anhydride, but not between carbamide and succinic anhydride, citraconic anhydride, or camphoric anhydride. W. P. S.

Phthalic Acid Derivatives; Constitution and Colour.
XVII. Tetrabromofluorescein, Tetrabromoeosin, and some of their Derivatives. DAVID S. PRATT, G. F. HUTCHINSON, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1293—1297).—Compare the analogous iodine compounds, A., 1918, i, 175. Tetrabromofluorescein, $\text{C}_{20}\text{H}_6\text{O}_5\text{Br}_4$, dissolves in alkali hydroxides with about the same colour as fluorescein, and is precipitated as a yellow *hydrate* on the addition of an acid. When this is dried in

a steam-oven, the brick-red, quinonoid form of tetrabromofluorescein is left, but this changes into the yellow, benzenoid form when wetted with acetone or ethyl acetate. The hydrate changes into the very pale yellow *tetrabromofluoresceincarbinolcarboxylic acid* when treated with alcohol, thus:



Anhydrous tetrabromofluorescein forms a bright red *diammonium* salt and a colourless *diacetate*, and reacts with bromine to give *octabromofluorescein* (tetrabromoeosin). This is almost colourless, but so sensitive to alkalis that it is generally faintly pink. It dyes silk an attractive pink shade, and forms a *diacetate*, crystallising with $1\text{C}_6\text{H}_6$, and a *tetra-ammonium* salt, of a brilliant, deep bronze colour, probably represented by the formula



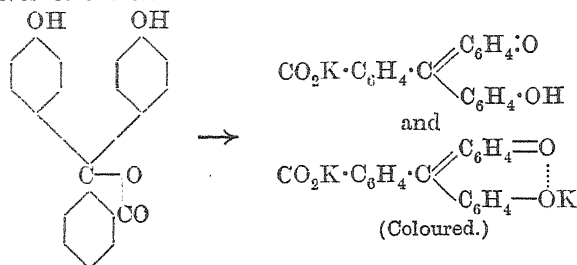
J. C. W.

Phthalic Acid Derivatives; Constitution and Colour.
XVI. Phenoltetrabromophthalein and some of its Derivatives. DAVID S. PRATT, F. B. DOANE, and A. W. HARVEY (*J. Amer. Chem. Soc.*, 1919, **41**, 1289—1293. Compare A., 1918, i, 167—172, 175—177, 540—541).—Tetrabromophthalic anhydride (*ibid.*, 540) condenses with phenol in the presence of fuming sulphuric acid (15% SO_3) to form *tetrabromofluoran*, $\text{C}_{20}\text{H}_8\text{O}_3\text{Br}_4$, colourless crystals, insoluble in alcohol, and a 75% yield of *phenoltetrabromophthalein*, $\text{C}_{20}\text{H}_{10}\text{O}_4\text{Br}_4$, which is nearly white, gives colourless solutions in most solvents, is indifferent to ammonia, but very sensitive to alkali hydroxides. The phthalein yields a colourless, crystalline *diacetate*, *dibenzoate*, and *dimethyl ether*, and may be brominated in boiling alcohol. *Tetrabromophenoltetrabromophthalein*, $\text{C}_{20}\text{H}_6\text{O}_4\text{Br}_8$, forms very pale yellow crystals, dissolves in alkali hydroxides with a brilliant blue colour, reacts with ammonia gas to give a turquoise-blue *diammonium* salt, and yields a colourless *diacetate* and *dibenzoate*, which both crystallise with one molecular proportion of benzene.

J. C. W.

The Quinone-Phenolate Theory of Indicators. The Reactions of Phenolsulphonphthalein and its Bromo- and Nitro-derivatives, and their Monobasic and Dibasic Salts. E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1919, **41**, 1190—1212. Compare A., 1918, ii, 328; this vol., ii, 400).—In the theory of indicators developed by Acree, it is held that the production of colour in the case of phenolphthalein does not begin when the lactone ring is opened, but when quinone-phenolate ions

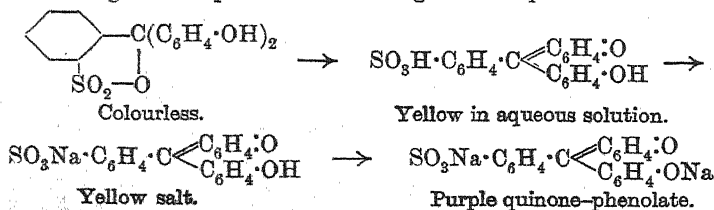
are formed. That is, phenolphthalein is regarded as a substance which gives colourless mono-acid and dark red di-acid salts, thus:



The existence of the intermediate salts has now been established in the case of phenolsulphonphthalein, and it is also shown that other factors than the further addition of alkali which tend to increase the production of quinone-phenolate ions, such as nitration or bromination of the indicator, operate to cause intense colour changes.

For the production of phenolsulphonphthalein, "saccharin" is hydrolysed by means of dilute hydrochloric acid (400 grams; 500 c.c. conc. HCl; 6—7 litres of water), and the ammonium hydrogen *o*-sulphobenzoic acid is allowed to crystallise after concentration (to 600 c.c.). The salt is finely powdered, thoroughly wetted with thionyl chloride, and heated for a few hours, when the excess of reagent is distilled off under reduced pressure and the residual cake is broken up and extracted with benzene. The pure *o*-sulphobenzoic anhydride is heated with phenol at 130—135° for six hours, when the excess of phenol is removed in steam, the residue is dissolved in alkali hydroxide, filtered, and the phenolsulphonphthalein is precipitated by an acid.

Phenolsulphonphthalein dissolves in boiling water to the extent of about 0.03 gram per 100 c.c. The solution is orange-coloured, since it contains the free quinonoid sulphonic acid. On the addition of pure sodium hydroxide solution, a purple streak appears locally, but this disappears on shaking, and is not permanent until nearly one equivalent of alkali has been added. That is, a salt of the quinonoid sulphonic acid is being formed having the same colour as the acid, and at last, when the ionisation of the sulphonic group is so depressed that phenolate ions appear, then the striking colour change takes place. The changes are represented thus:



The *mono-potassium*, *mono-silver*, and *mono-calcium* salts have been isolated; they all give orange solutions, which become purple

on the addition of alkali hydroxides. When left in an atmosphere of ammonia, phenolsulphonphthalein also forms an almost black *diammonium* salt, which dissolves with purple colour, and changes into a red *mono-ammonium* salt when left over sulphuric acid in a desiccator.

Tetrabromophenolsulphonphthalein is conveniently obtained by slowly adding bromine to a solution of the indicator in acetic acid maintained near its boiling point. The crystals are almost colourless when moistened with acetic acid, but acquire a flesh-pink colour when dried. When heated, it gives a green sublimate at 210° , becomes deeper orange in colour, and finally melts at $270\text{--}271^{\circ}$ (decomp.). The *di-ammonium* salt is stable in the neighbourhood of sulphuric acid, owing to the increased acidity of the phenol group. *Tetranitrophenolsulphonphthalein*, canary-yellow, minute flakes, decomp. above 200° , also forms a stable *di-ammonium* salt. The tetrabromo-compound dissolves in water (0.7 gram per litre), giving a dark red solution, which becomes deep blue on diluting or adding a trace of alkali, but gradually yellow on adding a strong acid. The tetranitro-compound gives purple-red solutions in water, which are not visually or spectroscopically altered by the addition of small amounts of alkali, but gradually become yellow on adding acids, the solution changing to purple once more on dilution. Owing to the presence of nitro-groups or bromine atoms in the phenolic components, the production of the coloured quinone-phenolate ions is rendered easy, and considerable concentrations of hydrogen ions must be present before their ionisation is depressed.

Phenolsulphonphthalein and its tetrabromide have been treated with diazomethane. The *products*, m. p. 158° and m. p. $234\text{--}235^{\circ}$, appear to be esters of the type $\text{SO}_3\text{Me}\cdot\text{C} \begin{smallmatrix} \nearrow \text{C}_6\text{H}_4\text{:O} \\ \searrow \text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$ but they are remarkably stable towards alkalis, and must be investigated more fully.

It is stated that stannic chloride is an excellent agent for the condensation of phthalic anhydride and phenols. J. C. W.

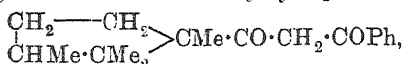
Optically Active Ketones : Ketones of 1:2:2:3-Tetramethylcyclopentane. H. RUPE and C. A. KLOPPENBURG (*Helv. Chim. Acta*, 1919, 2, 363—378).—1-Acetyl-1:2:2:3-tetramethylcyclopentane (1:2:2:3-tetramethylcyclopentyl methyl ketone),

$\text{CMe}_2 \begin{smallmatrix} \nearrow \text{CHMe}\cdot\text{CH}_3 \\ \searrow \text{CMeAc}\cdot\text{CH}_2 \end{smallmatrix}$, prepared by treating the chloride of campholic acid (1:2:2:3-tetramethylcyclopentane-1-carboxylic acid) with either zinc methyl or ethyl sodiomalonate or ethyl sodioacetate, and purified by means of its semicarbazone, is a colourless, mobile oil with a persistent cedar-wood oil odour, b. p. $93\text{--}95^{\circ}/10\text{ mm.}$, D_4^{20} 0.9163, $[\alpha]_D^{20} + 51.27^{\circ}$, $[\alpha]_D^{20} + 63.67^{\circ}$, $[\alpha]_{H\gamma}^{20}$ ($\lambda = 546.3\text{ }\mu\mu$) $+ 74.17^{\circ}$, and $[\alpha]_F^{20} + 93.32^{\circ}$; in benzene solution these rotations are respectively 43.45° , 53.89° , 62.06° , and 77.49° . The semicarbazone has m. p. 226° (decomp.) (Meerwein, this vol., i, 162, gave m. p. 232°); the *oxime*, m. p. 69.5° , the *p-nitrophenyl-*

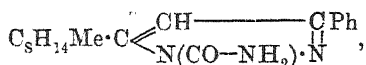
hydrazone, m. p. 134°, the *benzylidene* derivative, m. p. 45°, D_4^{20} 0.8896, $[\alpha]_D^{20} + 44.29^\circ$, $[\alpha]_B^{20} + 54.29^\circ$, $[\alpha]_{H_2O}^{20} + 61.49^\circ$, $[\alpha]_F^{20} + 69.36^\circ$ (in benzene), and the *anisylidene* derivative, m. p. 54°, D_4^{20} 0.8924, $[\alpha]_D^{20} + 50.65^\circ$, $[\alpha]_B^{20} + 63.43^\circ$, $[\alpha]_{H_2O}^{20} + 74.07^\circ$, $[\alpha]_F^{20} + 90.54^\circ$, were prepared.

1:2:2:3-Tetramethylcyclopentyl ethyl ketone, $C_{12}H_{22}O$, prepared by the action of either zinc ethyl iodide or zinc ethyl on the acid chloride of 1:2:2:3-tetramethylcyclopentane-1-carboxylic acid, forms a colourless oil of aromatic odour, b. p. 104°/10 mm., D_4^{20} 0.9124, $[\alpha]_D^{20} + 50.64^\circ$, $[\alpha]_B^{20} + 63.15^\circ$, $[\alpha]_{H_2O}^{20} + 73.89^\circ$, $[\alpha]_F^{20} + 94.08^\circ$. It does not condense with semicarbazide or hydroxylamine, but yields a *p*-nitrophenylhydrazone, m. p. 201°.

1-Benzoylacetyl-1:2:2:3-tetramethylcyclopentane,



prepared either by the condensation of ethyl 1:2:2:3-tetramethylcyclopentane-1-carboxylate with sodioacetophenone or by the action of ethyl benzoate on 1:2:2:3-tetramethylcyclopentyl methyl ketone, forms a viscous, yellow, odourless oil, b. p. 205°/10 mm., D_4^{20} 1.0500, $[\alpha]_D^{20} + 50.19^\circ$, $[\alpha]_B^{20} + 63.83^\circ$, $[\alpha]_{H_2O}^{20} + 76.08^\circ$, $[\alpha]_F^{20} + 100.92^\circ$; in benzene, the respective rotations are 45.07°, 57.26°, 68.22°, and 90.25°. Its alcoholic solution gives an intense red coloration with ferric chloride. With phenylhydrazine it forms the *diphenylated pyrazole*, $C_8H_{14}Me \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CPh} \\ \text{N} - \text{NPh} \end{smallmatrix}$ or $C_8H_{14}Me \cdot C \begin{smallmatrix} \text{CH} - \text{CPh} \\ \text{NPh} \cdot \text{N} \end{smallmatrix}$, which crystallises in long, white, felted needles, m. p. 142°, and becomes highly electrified when rubbed. With semicarbazide it gives the compound, $C_8H_{14}Me \cdot C \begin{smallmatrix} \text{CH} \cdot \text{CPh} \\ \text{N} - \text{N} \cdot \text{CO} \cdot \text{NH}_2 \end{smallmatrix}$ or



which forms short, apparently monoclinic, white prisms.

A simple method of preparing zinc methyl in large quantities by the action of a zinc-copper couple on methyl iodide in a steel bomb is described.

T. H. P.

Relations between the Ionones and Irone. L. RUZICKA (*Helv. Chim. Acta*, 1919, 2, 352—363).—The reduction of irone by hydrogen in presence of colloidal palladium or platinum black yields tetrahydroirone, an exact chemical proof being thus furnished of the presence of two double linkings in the irone molecule. According to the formulæ for α - and β -ionones and irone, the tetrahydro-derivatives of these compounds should be identical, except as regards optical activity. The two ionones do, indeed, yield the same tetrahydro-product (compare Skita, A., 1913, i, 63), but tetrahydroirone differs from this, not only by its dextro-rotation, but by its higher density and higher boiling point. Assuming the same structural formula, such differences can depend only on *cis*-

trans isomerism; the boiling-point difference, namely, $14^{\circ}/13$ mm., is higher than has been observed in any similar case, and may be conditioned by the relatively long side-chain of the molecules.

The attempts made to establish the structural relations between tetrahydroionone and tetrahydroirone have been unsuccessful. The latter does not undergo racemisation when heated at a high temperature with either hydrochloric acid or alkali. Further, oxidation of the saturated ketones by means of permanganate, as well as oxidation by means of sodium hypobromite of the sodium salts of tetrahydro-iononic and -ironic acids, do not yield the expected products, the formation of large proportions of oxalic acid in all cases indicating that the long side-chain is first oxidised away. Results previously obtained, especially the reaction by which β -ionone is formed, and which consists in the scission of a water molecule, indicate that in the ionones (and tetrahydroionone) the two side-chains, CH_3 and $\text{CH}:\text{CHAc}$, occupy *cis*-positions and in irone (and tetrahydroirone) *trans*-positions at the asymmetric carbon atom.

When irone is reduced in presence of colloidal palladium by means of a limited proportion of hydrogen, only tetrahydro- and not dihydro-irone is formed, and it is uncertain if Skita (*loc. cit.*) obtained dihydroionones in this way, no crystalline derivatives being described by him.

Tetrahydroirone, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2-\text{CMe}_2 \\ \text{CH}_2-\text{CHMe}\end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, forms a colourless oil of characteristic cedar-wood odour, b. p. $143^{\circ}/13$ mm., and in carbon disulphide solution decolorises bromine with evolution of hydrogen bromide. The *semicarbazone*, $\text{C}_{14}\text{H}_{27}\text{ON}_3$, forms crystals, m. p. 202° — 203° , and gives the ketone again when boiled with potassium hydrogen sulphate solution.

Tetrahydroionol, b. p. 142° — $143^{\circ}/17$ mm., D^{25}_D 0.9144 (Skita, A., 1916, i, 16, gave b. p. 142° — $143^{\circ}/20$ mm., D^{20}_D 0.9126), may be obtained by reducing the ionones by means of hydrogen in ethereal solution containing platinum black, whereas in presence of colloidal palladium the reduction proceeds only as far as tetrahydroionone.

Reduction of α -ionone in 50% aqueous-alcoholic solution by means of hydrogen in presence of Kelber's nickel catalyst (A., 1916, ii, 309) yields *dihydroionol* as an oil, b. p. 135° — 140° , so that in this case the reduction of the carbonyl group precedes that of one of the double linkings, probably that in the ring; this appears to be the first instance of such a reaction (compare Rupe, Werder, and Takagi, this vol., i, 27). Dihydroionol does not form a semicarbazone, and on oxidation is converted into *dihydroionone*, $\text{C}_{13}\text{H}_{22}\text{O}$, which is a mobile liquid, b. p. 130° — $132^{\circ}/14$ mm., and yields the *semicarbazide*, $\text{C}_{14}\text{H}_{25}\text{ON}_3$, m. p. 166° — 168° .

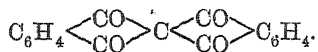
Tetrahydroironic acid, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2-\text{CMe}_2 \\ \text{CH}_2-\text{CHMe}\end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, has b. p. 185° — $190^{\circ}/15$ mm., m. p. (crude) about 80° , and *tetrahydroiononic acid*, of the same structural formula, is a viscous oil, b. p. 173° — $178^{\circ}/12$ mm.

T. H. P.

Diketohydrindene. III. ANANDA KISORE DAS and BROJENDRA NATH GHOSH (*J. Amer. Chem. Soc.*, 1919, **41**, 1221—1225. Compare T., 1915, **107**, 1442; 1916, **109**, 175).—When diketohydrindene is condensed with certain acid anhydrides in the presence of concentrated sulphuric acid, complex, sparingly soluble compounds are formed, which may also be prepared by condensing the anhydrides with anhydrobisdiketohydrindene (Wislicenus and Kötze, A., 1889, 1067), this being, therefore, the primary product in the first reaction. Thus, phthalic anhydride gives the compound, $C_{25}H_{12}O_8$, which crystallises from nitrobenzene in lustrous flakes, m. p. 320° ; benzoic anhydride yields the compound, $C_{25}H_{12}O_8$, golden-yellow needles, m. p. above 320° ; and succinic anhydride forms the compound, $C_{21}H_{10}O_2 \cdot H_2O$, which sublimes without melting at above 316° . The compounds dissolve in hot aniline without forming anilides.

The condensation of diketohydrindene with phthalic anhydride in the presence of acetic anhydride has been described by Marchese (A., 1907, i, 941), who obtained a compound, $C_{26}H_{12}O_8$. This is similar to the above compound, $C_{25}H_{12}O_8$, in outward appearance and m. p., but it differs in that it dissolves freely in sodium hydroxide and is changed on boiling with aniline into a black, crystalline substance, $(C_8H_6O)_x$, m. p. 110° .

The experiment with phthalic anhydride was undertaken in the hope of obtaining a compound of the formula



To this end, ethyl phthalate was made to react with diketohydrindene in the presence of sodium ethoxide, but the product was Schwerin's 2-benzoyl-1:3-diketohydrindene (A., 1894, i, 194) mixed with a little anhydrobisdiketohydrindene. J. C. W.

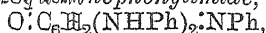
Indophenols and Indamines. II. GUSTAV HELLER (*Annalen*, 1919, **418**, 259—274. Compare A., 1912, i, 916).—It has long been known that indophenols are decomposed by hot dilute mineral acids in the sense of the equation $O:C_6H_4:N \cdot C_6H_4 \cdot OH + H_2O = O:C_6H_4 \cdot O + NH_2 \cdot C_6H_4 \cdot OH$. A further change occurs, however, when contact with the mineral acid is maintained for many hours, $2O:C_6H_4 \cdot O + 2NH_2 \cdot C_6H_4 \cdot OH = C_6H_4(OH)_2 + O:C_6H_2(NH \cdot C_6H_4 \cdot OH)_2 \cdot O$,

so that the final main products are quinol and dianilinoquinones. The complex substance obtained by the action of hydrochloric acid on the simplest indophenol (*loc. cit.*) is now shown to be 2:5-di-*p*-hydroxyanilino-*p*-benzoquinone by its formation from *p*-benzoquinone and *p*-aminophenol in aqueous-alcoholic solution. In a similar manner, toluquinone yields di-*p*-hydroxyanilino-toluquinone, brown needles, which do not melt below 290° , and *p*-benzoquinone and *as*-dimethyl-*p*-phenylenediamine yield 2:5-di-*p*-dimethylaminobenzoyl-*p*-benzoquinone. The last compound is not obtained in the decomposition of phenol-blue by hydrochloric acid, because the

dimethylamino-group is replaced by hydroxyl and 2:5-di-*p*-hydroxylanilino-*p*-benzoquinone is formed.

The course of the decomposition of indophenols described above was first elucidated by an investigation of the action of hydrochloric acid (*N*/5) on Bamdrowski's base, *p*-benzoquinone-*p*-tolylimide, $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{C}_7\text{H}_7$, whereby quinol and 2:5-di-*p*-toluidino-*p*-benzoquinone were obtained.

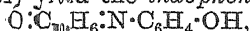
2:5-Dianilino-*p*-benzoquinonephenylimide,



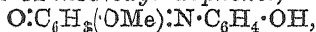
m. p. 202—203°, and 2:5-dianilino-*p*-benzoquinone-*p*-tolylimide, reddish-brown leaflets, m. p. 214°, are obtained by treating *p*-benzoquinonephenylimide and *p*-benzoquinone-*p*-tolylimide respectively with an alcoholic solution of aniline containing a little acetic acid.

After contact with dilute sulphuric acid for three days, Bindscheller's green yields, amongst other products of the decomposition, tetramethylbenzidine, produced probably by the oxidising action of *p*-benzoquinone on dimethylaniline formed in the reaction.

By oxidation with an alkaline solution of sodium hypochlorite at -10° to -15° , α -naphthol and *p*-aminophenol (but not phenol and 4-amino- α -naphthol) yield the indophenol,



crystalline powder, which forms two isomeric monoanilino-derivatives, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$, m. p. 255° and 181° respectively; guaiacol and *p*-aminophenol yield 11-methoxyindophenol,

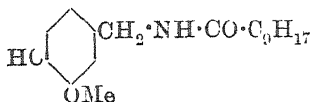


m. p. 181—182° (decomp.) (9:12-dianilino-derivative, m. p. 208—209°), and *m*-chlorophenol and *p*-aminophenol yield 1-chloroindophenol, m. p. 156° (sodium derivative, $\text{C}_{12}\text{H}_7\text{O}_2\text{NClNa}$, needles); the dianilino-derivative, $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_2\text{Cl}$, bronze-green needles, m. p. 211—212°, of the last compound is oxidised in alcoholic solution at 60° to the dianil, red prisms, m. p. 212—213°, by chromic and acetic acids.

4-Anilino-4'-hydroxydiphenylamine, $\text{NHPh}:\text{C}_6\text{H}_4:\text{NH}:\text{C}_6\text{H}_4:\text{OH}$, silvery scales, m. p. 145°, is obtained by heating a mixture of 4-aminodiphenylamine, quinol, and zinc chloride at 180°; a portion of the product can be purified by crystallisation, but the main portion, apparently in consequence of oxidation, must be reduced in alcoholic solution by zinc dust and glacial acetic acid before it is recrystallised. By treating its solution in boiling benzene with mercuric oxide, the substance is oxidised to 3-anilinoindophenol, $\text{O}:\text{C}_6\text{H}_4:\text{N}:\text{C}_6\text{H}_4:\text{NHPh}$, bluish-violet crystals containing 1 mol. CHCl_3 , m. p. 158°. C. S.

The Constitution of Capsaicin, the Pungent Principle of Capsicum. E. K. NELSON (*J. Amer. Chem. Soc.*, 1919, 41, 1115—1121).—The amount of capsaicin in cayenne pepper varies considerably, a very good sample yielding, when treated according to Micko's method (A., 1899, i, 716; see also Nelson, A., 1911, ii, 551), about 60 grams of the pure substance per 50 kilos.

The compound is now shown to be a condensation product of vanillylamine and a decenoic acid (annexed formula).



Capsaicin crystallises from a mixture of light petroleum and ether (9:1) in monoclinic plates (α , 1.520; β , 1.540; γ , 1.580), m. p. 65°. Its methyl ether forms bundles of minute needles (α , 1.55; β , 1.58; γ , 1.60), m. p. 77–78°, and is only slightly pungent. On oxidation with alkaline permanganate, this ether yields veratric acid, and when hydrolysed by means of methyl-alcoholic hydrochloric acid, it gives 3:4-dimethoxybenzylamine hydrochloride, which crystallises in monoclinic rods or narrow plates (α , 1.505; β , 1.670; γ , 1.700) (compare Juliusberg, A., 1907, i, 219). Capsaicin itself yields 4-hydroxy-3-methoxybenzylamine hydrochloride (see below) when hydrolysed in the same way, but hydrolysis with 25% sodium hydroxide at 180° enables the acid fragment to be isolated in excellent yield. The alkaline liquid is saturated with carbon dioxide, extracted with ether to remove the decomposition products of the amine residue, the aqueous portion is then evaporated to dryness, the organic salt is separated by means of boiling alcohol, and finally decomposed by dilute sulphuric acid. The acid appears to be a new *decenoic acid*, $\text{C}_{10}\text{H}_{18}\text{O}_2$. It has m. p. –5°, b. p. 258–261°/atm. (corr.), forms a *dibromide*, m. p. 57–59°, and an *amide*, pearly leaflets, m. p. 96–97° (corr.), which differs from the amides of two decenoic acids described by Wallach, and the saturated *decoic acid* obtained by Paal's method has b. p. 260°, m. p. 24–25°, and immediately causes the liquefaction of decoic acid from coconut oil (compare Lapworth and Royle, T., 1919, 115, 1109).

The base, *vanillylamine* (4-hydroxy-3-methoxybenzylamine), was prepared for comparison by the reduction of vanillin oxime. It is very unstable, crystallises from water in slender needles, m. p. 131–133° (after drying at 110°), and yields a *hydrochloride*, colourless rods (α , 1.510; β , 1.705; γ , 1.735). J. C. W.

Solubility of Carbon Dioxide in Solutions of Chlorophyll.

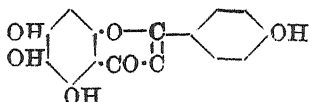
ROBERT KREMANN and NORBERT SCHNIDERSCHITSCH (*Monatsh.*, 1916, 37, 659–679).—With the object of ascertaining whether chlorophyll and carbon dioxide form an additive compound in the assimilation of the latter by the leaves of trees, the authors have determined the solubility of carbon dioxide in 95% alcoholic solutions of chlorophyll both in the absence and the presence of light. The experiments were carried out both by the static method and the dynamic method. In the latter method, the amount of carbon dioxide dissolved was estimated by determinations of the electrical conductivity of the solutions. A similar series of experiments was also carried out with 95% alcohol which contained no chlorophyll. The experiments show that the solubility of carbon dioxide in alcohol and in alcoholic solutions of chlorophyll is practically the same. It must therefore be concluded that neither in the dark nor in daylight is there a measurable formation of an additive compound

between carbon dioxide and chlorophyll. Further, no such compound could be observed in a colloidal suspension of chlorophyll in 45% alcohol through which carbon dioxide had been bubbled. Consequently, if such an additive compound takes any part in the absorption of carbon dioxide by living leaves, this compound can only be present in an almost unrecognisable quantity. J. F. S.

The Tannin of the Knopper Gall. MAXIMILIAN NIERENSTEIN (T., 1919, 115, 1174—1180).

5:6:7-Trihydroxyflavone: Constitution of Scutellarein.

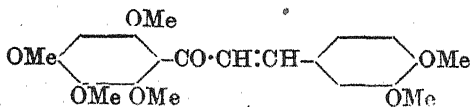
G. BARGELLINI (*Gazzetta*, 1919, 49, ii, 47—63).—The fact that scutellarein alone is obtained by the action of hydriodic acid on 2:3:4:6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone, which thus undergoes demethylation and also loses 1 mol. of water, indicates that scutellarein is either 5:7:8:4'- or 5:6:7:4'-tetrahydroxyflavone (A., 1915, i, 84). The decision between these two constitutions is now made as follows. By condensation with methyl benzoate in presence of sodium, 2:3:4:6-tetramethoxyphenyl methyl ketone is converted into 2:3:4:6-tetramethoxyphenyl benzoylmethyl ketone, and hydrolysis of the latter by means of hydriodic acid, as above, yields a trihydroxyflavone, which may be either the 5:7:8- or the 5:6:7-derivative; as this compound is different from the 5:7:8-trihydroxyflavone (hydroxychrysin) described by Nierenstein (A., 1912, i, 292), it must be regarded as 5:6:7-trihydroxyflavone. On the assumption that the elimination of water in the formation of scutellarein from 2:3:4:6-tetramethoxyphenyl *p*-methoxybenzoylmethyl ketone takes place similarly to the elimination of water from benzoylmethyl 2:3:4:6-tetramethoxyphenyl ketone, scutellarein must be regarded as 5:6:7:4'-tetrahydroxyflavone (annexed formula).



Melting points different from those obtained by the author have been given by Nierenstein for certain of

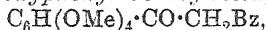
these derivatives. Thus, for 2:3:4:6-tetramethoxyphenyl methyl ketone, the author finds m. p. 48—50°, and Nierenstein (T., 1917, 111, 4) 92—93°, and, in view of the ease with which *O*-methylated derivatives are formed when phloroglucinol and its derivatives, and also 1:2:3:5-tetrahydroxybenzene and its derivatives, are methylated, it may be that Nierenstein's so-called 2:3:4:6-tetramethoxyphenyl methyl ketone, prepared by direct methylation of the corresponding tetrahydroxy-compound, is in reality a *C*-methylated derivative.

2:3:4:6:3':4'-Hexamethoxyphenyl styryl ketone (annexed formula), obtained by condensation of 2:3:4:6-tetramethoxyphenyl methyl ketone with veratraldehyde, is a pale yellow compound, m. p. 127—128°, and dissolves in concentrated sulphuric acid with an intense red coloration.



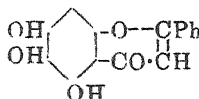
Nierenstein (*loc. cit.*) describes 2-hydroxy-3:4:6-trimethoxyphenyl methyl ketone, m. p. 125—126°, and 6-hydroxy-2:3:4-trimethoxyphenyl methyl ketone, m. p. 164—165°. The trimethylated derivative prepared by the author has m. p. 106—108°, and is probably the former of these compounds; its *acetyl* derivative, m. p. 106°, and its *benzoyl* derivative, m. p. 120—122°, have been prepared. With veratraldehyde in presence of sodium hydroxide, it yields 2-hydroxy-3:4:6:3':4'-pentamethoxyphenyl styryl ketone, m. p. 143°, as described by Nierenstein. The latter describes 2:6-dihydroxy-3:4-dimethoxyphenyl methyl ketone, m. p. 166—168°, whereas the dimethylated derivative obtained by the author has m. p. 162—163°; its *acetyl* derivative, m. p. 110—112°, has also been prepared. The tetra-, tri-, and di-methyl compounds all dissolve in concentrated sulphuric acid, giving a yellow coloration, changing to brownish-green and then to bluish-violet on heating; this colour reaction is probably common to all derivatives of 1:2:3:5-tetramethoxybenzene.

2:3:4:6-Tetramethoxyphenyl benzoylmethyl ketone,



forms yellow, prismatic crystals, m. p. 110—112°, and in alcoholic solution gives an intense red coloration with ferric chloride; a crystal of the compound is coloured red by concentrated sulphuric acid, the latter becoming yellow.

5:6:7-Trihydroxyflavone (annexed formula) forms a brownish-yellow powder, m. p. about 260° (decomp.), or,



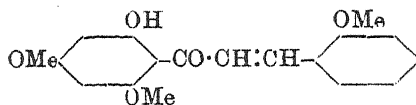
when prepared from the di- or tri-*acetyl* derivative, shining, yellow crystals, turning brown locally at 240—250°, m. p. 262—266°. It dissolves in aqueous borax to an intense yellow solution, in concentrated sulphuric acid to a yellow solution, in sodium hydroxide solution, giving a reddish-brown solution, and in sodium carbonate solution, giving a green solution turning brownish-red. Addition of a few drops of concentrated sulphuric acid to a hot solution of the compound in glacial acetic acid yields a red, crystalline compound similar to that given under these conditions by scutellarein. Addition of a little sodium amalgam to the alcoholic solution of the trihydroxyflavone results in the deposition of green flocks; scutellarein behaves similarly, whereas 5:7:4'-trihydroxyflavone (apigenin) and 6:7-dihydroxyflavone give red colorations, and 5:7:3':4':5'-pentahydroxyflavone reddish-brown flocks. Thus, the formation of green flocks with sodium amalgam is probably a reaction characteristic of flavones containing three vicinal hydroxyl groups in the benzopyrone nucleus, and may be of service as an indication of the constitution of other natural flavones or flavonols. The *diacetyl* derivative of 5:6:7-trihydroxyflavone, $\text{C}_{19}\text{H}_{14}\text{O}_7$, forms yellow needles, m. p. 198—200°, and gives a red coloration with ferric chloride in alcoholic solution. The *triacetyl* derivative, $\text{C}_{21}\text{H}_{16}\text{O}_8$, forms white needles, m. p. 190—192°, and dissolves in concentrated sulphuric acid to a yellow solution, but gives no coloration with ferric chloride in alcoholic solution. The (6:7-?) *dimethyl ether*,

$C_{17}H_{11}O_5$, forms yellow needles, m. p. 155—156°, and with ferric chloride in alcoholic solution gives a red coloration changing to green with excess of the reagent. The *trimethyl ether*, $C_{18}H_{16}O_5$, forms light, wool-like needles, m. p. 165—166°, and dissolves to a yellow solution in concentrated sulphuric acid, but gives no coloration with ferric chloride in alcoholic solution. T. H. P.

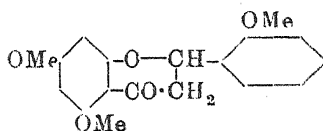
5:7:2'-Trihydroxyflavanol: Synthesis of Datiscetin.

G. BARGELLINI and E. PERATONER (*Gazzetta*, 1919, **49**, ii, 64—69). —5:7:2'-Trihydroxyflavanol has been prepared as follows. Condensation of 2-hydroxy-4:6-dimethoxyphenyl methyl ketone with the methyl ether of salicylaldehyde in presence of sodium hydroxide yields 2-hydroxy-4:6:2'-trimethoxyphenyl styryl ketone, which, when boiled with dilute hydrochloric acid in alcoholic solution, is converted partly into 5:7:2'-trimethoxyflavanone. Treatment with amyl nitrite transforms the latter into its *isonitroso*-derivative, and this, when heated with dilute sulphuric acid in acetic acid solution, gives 5:7:2'-trimethoxyflavanol. The latter should be identical with the trimethyl ether of the datiscetin of Marchlewski and Korczyński (A., 1907, i, 435), and should yield datiscetin (5:7:2'-trihydroxyflavanol) when treated with hydriodic acid, but lack of material has prevented the completion of the work.

2-Hydroxy-4:6:2'-trimethoxyphenyl styryl ketone (I) forms



(I.)



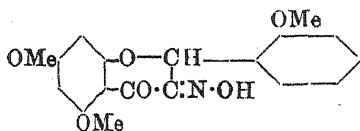
(II.)

canary-yellow crystals, m. p. 106—108°, and dissolves in concentrated sulphuric acid with an orange-red coloration.

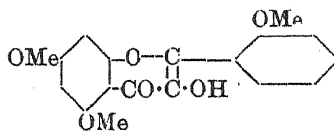
5:7:2'-Trimethoxyflavanone (II) crystallises in white needles, m. p. 124—125°, and dissolves in concentrated sulphuric acid to a brownish-yellow solution.

2-Oxamino-5:7:2'-trimethoxyflavanone (III) forms pale yellow crystals, m. p. 189—190° (decomp.).

5:7:2'-Trimethoxyflavanol (IV) crystallises in pale yellow



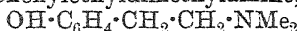
(III.)



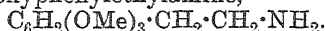
(IV.)

needles, m. p. 158—160°, and dissolves in concentrated sulphuric acid, giving a yellow solution which exhibits intense green fluorescence. Datiscetin also gives a fluorescent solution in sulphuric acid. T. H. P.

The Anhalonium [Cactus] Alkaloids. I. Anhaline and Mezcaline. ERNST SPÄTH (*Monatsh.*, 1919, 40, 129—154).—The cactus alkaloids have been investigated most completely so far by Heffter (A., 1895, i, 120; 1896, i, 267; 1898, i, 499; 1901, i, 736; 1905, i, 877), and seven bases are described in the literature, namely, anhaline, mezcaline, pellotine, anhalonidine, anhalonine, anhalamine, and lophophorine. These have about the same physiological properties (Mogilewa, *Arch. expt. Path. Pharmac.*, 1903, 49, 137) and are closely related chemically. It is now shown that anhaline is identical with the hordenine of barley germs, that is, it is β -*p*-hydroxyphenylethyldimethylamine,

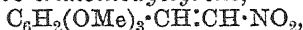


(Léger, A., 1906, i, 204, 761; Rosenmund, A., 1910, i, 241), and mezcaline has been synthesised by a method which shows that it is β -3:4:5-trimethoxyphenylethylamine,

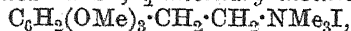


Anhalonine and lophophorine each contain a methoxy-group and two non-hydroxylic oxygen atoms, but the other bases are simply methylated members of the 3:4:5-trihydroxyphenylethylamine series.

Synthesis of Mezcaline.—Gallic acid is methylated by means of methyl sulphate, and then converted into 3:4:5-trimethoxybenzoyl chloride by the action of phosphorus pentachloride. This is reduced in boiling toluene by hydrogen in the presence of palladinised barium sulphate, the yield of 3:4:5-trimethoxybenzaldehyde being good, although some by-products are formed (Rosenmund, A., 1918, i, 300). The aldehyde is condensed with nitromethane to form ω -nitro-3:4:5-trimethoxystyrene,



long, yellow needles, m. p. 120—121°, and this is reduced by means of zinc dust and acetic acid to an oxime, and then by sodium amalgam to β -3:4:5-trimethoxyphenylethylamine, which is a colourless, highly refractive, viscous oil having b. p. 180—180.5°/12 mm. and a faint, basic odour. The procedure at all these stages is that devised by Rosenmund (A., 1910, i, 110). The base gives the following derivatives, which are identical with those obtained from a specimen of Merck's mezcaline, and already described in part by Heffter; *sulphate*, $\text{B}_2\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, long, glistening prisms, m. p. 183—186°; *picrate*, yellow crystals, m. p. 216—218°; *platinichloride*, rosettes of straw-yellow needles, m. p. 187—188°; *aurichloride*, $\text{B}_2\text{HAuCl}_4\cdot\text{H}_2\text{O}$, orange needles, decomp. 140—141°; *benzoyl* derivative, m. p. 120—121°; *m*-nitrobenzoyl derivative, m. p. 161—162°; *quaternary methiodide*,



m. p. 224—225°.

Heffter found on analysis that mezcaline behaves as though it contains a methylamino-group, —NHMe , and this is confirmed. The explanation seems to be that some rearrangement in the molecule proceeds during the analysis, for Heffter himself disposed of the alternative formula, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CH}_2\cdot\text{NHMe}$. Still another alternative, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CHMe}\cdot\text{NH}_2$, is now negatived by the

synthesis of the base with this formula. 3:4:5-Trimethoxyphenyl methyl ketone (Mauthner, A., 1910, i, 680) is converted into the *oxime*, needles, m. p. 102—103°, and this is reduced by means of sodium amalgam. α -3:4:5-Trimethoxyphenylethylamine is a strong base which forms a solid carbonate on exposure to the air. Its *benzoyl* derivative has m. p. 150—151°, and the *quaternary methiodide*, $C_6H_2(OMe)_3 \cdot CHMe \cdot NMe_3I$, melts at 180—182°, then resolidifies, melts again at 235—237°, and decomposes at 250—255°.

J. C. W.

Some Cases of Solubility Influence. II. Compounds of Caffeine existing in Aqueous Solution. G. BARGELLINI (*Gazzetta*, 1919, 49, i, 191—200).—Cryoscopic investigation of solutions containing caffeine, together with either antipyrine, sodium benzoate, resorcinol, quinol, or catechol gives results indicating the formation of compounds between the solutes, the solubility of the caffeine being apparently increased. With phloroglucinol or pyrogallol, however, caffeine appears to form compounds exhibiting but slight solubilities in water (compare Ultée, A., 1910, i, 132). The solubility of caffeine in water is about 1%, in 10% resorcinol solution about 3%, and in more concentrated resorcinol solutions still more.

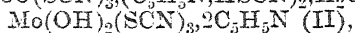
T. H. P.

Compound of Yohimbine containing Arsenic. W. GRÜTEFFIEN (U.S. Pat. 1305462).—Arsenic (150.7 parts) and yohimbine (368 parts) are dissolved in water (1000 parts). The solution is filtered and evaporated, the residue is mixed with acetone, and the salt thus obtained is filtered and dried at 100°. *Yohimbine arsenate* thus produced forms an almost colourless powder, m. p. 243°. *Yohimbine methylarsinate*, m. p. 203°, is obtained from methylarsinic acid (130 parts) and yohimbine (368 parts). *Yohimbine phenylarsinate*, m. p. about 140°, is produced by the interaction of phenylarsinic acid (202 parts) and yohimbine (368 parts) dissolved in alcohol (1000 parts). *Yohimbine chloroarsenobehenolate* is a faintly coloured powder, m. p. about 90°, soluble in water, alcohol, and acetone. It is produced from chloroarsenobehenolic acid (462.5 parts) and yohimbine (368 parts) dissolved in acetone (10,000—15,000 parts). If necessary, the solution is filtered and the filtrate carefully evaporated. The viscous paste which is at first obtained becomes solid after keeping for a short time in a desiccator, and can then be easily pulverised. These compounds are stated to be especially suitable as therapeutic agents because they do not possess the pronounced irritating effect on the intestine which is common both to arsenic compounds generally and to yohimbine.

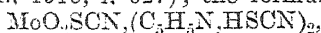
CHEMICAL ABSTRACTS.

Colour Reactions of Molybdenum and Tungsten. I. G. A. BARBIERI (*Atti R. Accad. Lincei*, 1919, [v], 28, i, 351—355).—According to Sand and Burger (A., 1905, i, 923; 1906, i, 487), and Rosenheim and Koss (A., 1906, i, 603), the action of pyridine on the red and violet liquids obtained from an acidified solution

containing a molybdate and a thiocyanate, either by boiling or by treating in the cold with zinc, tin, or other reducing agent, yields the compounds $\text{MoO}(\text{SCN})_3, (\text{C}_5\text{H}_5\text{N}, \text{HSCN})_2, \text{H}_2\text{O}$ (I) and

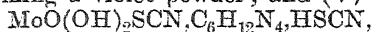


the molybdenum being quinquivalent. Since compound II is formed in acid solution, it is more probable that the pyridine unites with the thiocyanic acid, and that the molybdenum exists as molybdy, MoO_2 (A., 1916, i, 627); the formula,



for this compound would explain also its conversion into compound I by treatment with thiocyanic acid.

When molybdic acid is reduced in presence of thiocyanic acid (Braun's reaction, *Zeitsch. anal. Chem.*, 1863, **2**, 36), the colorations produced may be due partly to sexa- and partly to quinquivalent molybdenum. The latter alone is present in molybdenyl ammonium chloride, $\text{MoOCl}_3, 2\text{NH}_4\text{Cl}$, which gives an orange-red coloration when treated, in a solution acidified with hydrochloric acid, with excess of ammonium thiocyanate; the colour changes to blood-red and then to violet on dilution or heating, further addition of water producing in succession orange-yellow and yellow colorations, and finally decolorisation. The different colours are hence the result of hydrolysis. The orange-yellow liquid gives with pyridine thiocyanate the compound I (above), whilst treatment of the coloured solutions with a hexamethylenetetramine salt under definite experimental conditions gives the compounds: (III) $\text{Mo}(\text{OH})_2(\text{SCN})_3, \text{C}_6\text{H}_{12}\text{N}_4, \text{HSCN}, 2\text{H}_2\text{O}$, black, prismatic crystals; (IV) $\text{Mo}(\text{OH})_3(\text{SCN})_2, \text{C}_6\text{H}_{12}\text{N}_4, \text{HSCN}, 2\text{H}_2\text{O}$, blackish-green crystals forming a violet powder; and (V)



orange-yellow prisms. Compounds III and IV give violet alcoholic solutions which become orange-yellow when diluted with water and heated, and, on cooling, then deposit compound V; treatment of the latter with thiocyanic acid yields a violet solution.

T. H. P.

Synthetic Investigations in the Quinine Series. I. Synthesis of β -Collidine [4-Methyl-3-ethylpyridine]. L. RUZICKA and V. FORNASIR (*Helv. Chim. Acta*, 1919, **2**, 338—348). —The authors have succeeded in synthesising β -collidine [4-methyl-3-ethylpyridine], the various steps in the process being as follows: (1) Preparation of 2:6-dihydroxy- β -collidine, either by heating γ -cyano- β -methyl- α -ethylglutaconimide (5-cyano-2:6-dihydroxy-4-methyl-3-ethylpyridine) (compare Guareschi, A., 1897, i, 168) with hydrobromic acid, or by condensing ethyl ethylacetoacetate with ethyl cyanoacetate in presence of sodium and treating the cyano-glutaconic ester thus obtained with sodium hydroxide (compare Rogerson and Thorpe, T., 1905, **87**, 1685); (2) conversion of the 2:6-dihydroxy- β -collidine into 2:6-dichloro- β -collidine by means of phosphoryl chloride; and (3) removal of the chlorine atoms by treatment with hydriodic acid, monochloro- β -collidine, and then β -collidine, being formed.

γ -Cyano- β -methyl- α -ethylglutaconimide has m. p. about 220° (crude) (Guareschi, *loc. cit.*, gave 234°), and its ammonium derivative, m. p. about 315° (Guareschi gave m. p. about 300°).

2:6-Dichloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \swarrow CCl \cdot CEt \\ \searrow CCl : CH \end{smallmatrix} > CMe$, is a colourless, mobile oil, b. p. 140°/12 mm., having a piercing odour and an inflammatory action on the skin.

2-Chloro-4-methyl-3-ethylpyridine, $N \begin{smallmatrix} \swarrow CCl \cdot CEt \\ \searrow CH = CH \end{smallmatrix} > CMe$, forms a colourless, mobile oil with the odour of pyridine, b. p. 110°/12 mm. Its *picrate* has m. p. about 110°. T. H. P.

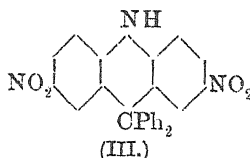
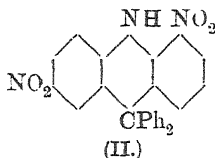
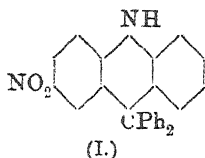
Compounds of 2-Phenylquinoline-4-carboxylic Acid with Halogen Acids. H. W. RHODEHAMEL (U.S. Pat. 1306439).—Compounds of 2-phenylquinoline-4-carboxylic acid with halogen acids are prepared by mixing the parent materials, using an excess of halogen acid, and then removing the excess of the latter by drying. The *hydriodide* forms orange-yellow crystals, m. p. 243°. It is useful as a therapeutic agent for rheumatism and gout. The *hydrobromide* forms brownish-yellow crystals, m. p. 255°. The *hydrochloride*, m. p. 223°, and *hydrofluoride* form lemon-yellow crystals. CHEMICAL ABSTRACTS.

Nitro-derivatives of 5-Diphenyldihydroacridine. F. KEHRMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, **2**, 315—323. Compare A., 1918, i, 311; ii, 344).—In presence of acids, 5-diphenyldihydroacridine (compare Baeyer and Villiger, A., 1904, i, 898) is readily oxidised at the ordinary temperature by various oxidising agents, yielding coloured products with the characters of salts; the study of these products is attended with considerable difficulty. By nitric acid diluted largely with glacial acetic acid, 5-diphenyldihydroacridine is energetically attacked, with formation of crystalline nitro-derivatives, of which six have been isolated pure (see below). The corresponding amino-derivatives behave towards oxidising agents like the leuco-compounds of colouring matters, showing the characteristic properties of quinoneimide dyes and resembling particularly many azoxine dyes. The behaviour of the nitro-derivatives towards alcoholic alkali hydroxide accords with the assumption that at least one nitro-group occupies the para-position with respect to the ter-valent ring nitrogen atom; they dissolve in the alkali, yielding pronounced green, red, and blue colorations, thus resembling closely the analogous nitro-derivatives of phenazoxine and thiodiphenylamine.

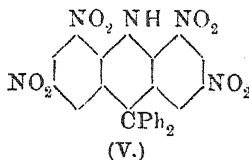
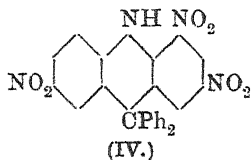
The *mononitro*-derivative of 5-diphenyldihydroacridine (I) forms compact, many-faced crystals with the colour of crystalline potassium dichromate, or, when ground, a pale orange powder, m. p. 300—301°; concentrated sulphuric acid dissolves and decomposes it, with formation of a deep blue coloration. Its *acetyl* derivative forms large, four-sided plates, m. p. 215°, yielding an

almost white powder. Addition of alkali hydroxide solution to the hot alcoholic solution yields a dichroic liquid, which is greenish-yellow in thin and purple-red in thick layers.

The *dinitro*-derivative A (formula II), forms heavy, orange-



yellow, many-faced crystals, m. p. 287—288°, giving a golden-yellow powder; its solution in alcoholic sodium hydroxide is greenish-yellow in thin and violet-brown in thick layers. The *dinitro*-derivative B (formula III) forms compact, lemon-yellow crystals with a slight blue reflex and a yellow powder with a green tinge; it begins to decompose at about 300° and has m. p. about 322.5°. Its alcoholic alkali hydroxide solution is blue in thin and deep purple in thick layers.



The *trinitro*-derivative (formula IV) forms orange-yellow leaflets containing benzene of crystallisation and a golden-yellow powder, m. p. 257—258°; its solution in alcoholic alkali hydroxide is magenta-red, and becomes reddish-violet on addition of a little water, whilst much water forms a yellow, flocculent precipitate.

The *tetranitro*-derivative (formula V) forms pale orange-yellow needles and a pale yellow powder, m. p. about 180°; in alcoholic alkali hydroxide it gives a magenta-red solution, changing to violet on dilution.

The *hexanitro*-derivative (formula VI) forms granular, yellow crystals, m. p. 317—318° (decomp.), and dissolves in alcoholic alkali hydroxide to a magenta-red liquid, the colour of which is unchanged by dilution.

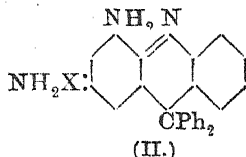
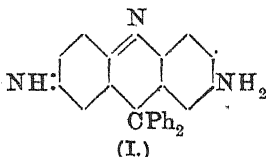
T. H. P.

Carbazine Dyes, a New Class of Quinone-imide Derivatives. F. KEHRMANN, HENRI GOLDSTEIN, and PETER TSCHUDI (*Helv. Chim. Acta*, 1919, 2, 379—397).—The amines obtained by reduction of the nitro-derivatives prepared from 5-diphenyldi-hydroacridine (preceding abstract) behave as the leuco-compounds of dyes into which they are transformed by oxidation. Owing to their evident analogy to azoxine and thiazine dyes, the name

carbazine is given to these dyes. Despite their relation to acridine, carbazine dyes exhibit little similarity to the acridine dyes, the dissimilarity being sufficiently explained by the difference between the chromophores in the two cases. Like the azine, azoxine, and thiazine dyes, carbazine dyes are derivatives of quinone-di-imide, this relationship being fully borne out by their properties.

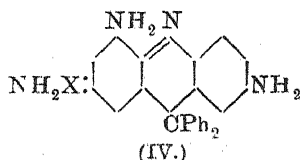
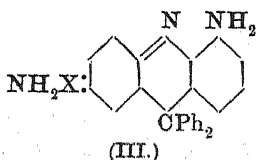
The introduction of an amino-group is accompanied by the following colour changes in the mono-acid salts: with carbazine [dihydroacridine], from yellow to bluish-green; with azoxine, from yellowish-red to bluish-violet; with thiazine, from violet-red to violet-blue, and with safranine, from violet-red to scarlet. The absolute value of the bathochromic or hypsochromic effect produced by the introduction of an amino-group into a chromogen is in general a function of the basicity of the complex it enters, the action being the more strongly bathochromic the less this basicity is developed. Thus, to explain the conversion of the bluish-green malachite-green into the bluish-violet crystal-violet by the introduction of a second *p*-dimethylamino-group, the hypothesis of colours of the second order is unnecessary. Indeed, whether the introduction of amino-groups into coloured complexes produces deepening of the colour or the reverse depends primarily on the chemical nature of the complex and secondarily on the positions assumed by the entering groups.

The quinone-imide base (formula I), corresponding with the



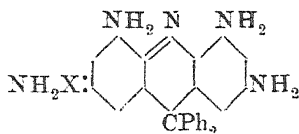
bluish-green mono-acid salts mentioned above, is yellowish-red in ethereal solution and shows a pronounced yellow fluorescence; even ammonium carbonate separates it completely from its salts. Oxidation by means of ferric chloride of the colourless leuco-diamine prepared by reduction of the yellowish-red dinitro-compound (*loc. cit.*) yields a dye (formula II or III), which, as mono-acid salt, is deep olive-green; the corresponding dark cherry-red base is even weaker than the preceding, as its salts are decomposed by sodium acetate.

Reduction of the trinitro-compound (*loc. cit.*) yields a colourless leuco-triamine, which is oxidised by ferric chloride to a colouring matter (formula IV) with an intense, pure violet mono-acid

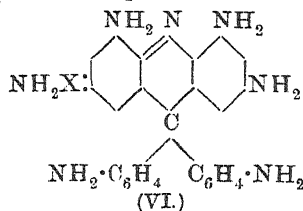


salt; the base, which is separated from its salts by ammonia, but only incompletely by ammonium carbonate, is deep orange-red, but non-fluorescent in ethereal solution. Hence the first amino-group exerts a bathochromic, but the second a hypsochromic, influence, with the limitation that the colour strength is considerably increased. Comparative dyeing tests with tannin-mordanted cotton show that the colour strength increases from the chromogen to the violet diamine, and then gradually falls until the pentamine is reached.

The leuco-tetramine gives on oxidation a pure blue mono-acid salt of the probable formula V, and the hexamine one of the probable formula VI, also blue. With both salts correspond imide bases.



(V.)

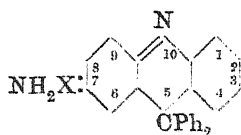


(VI.)

which are liberated from their salts only by the strongest inorganic bases, that derived from the hexamine only incompletely; boiled distilled water extracts the blue hydrates quantitatively from the violet-red ethereal solutions.

By excess of more or less concentrated acids, all the colouring matters are converted into poly-acid salts of different colour, these being mostly hydrolysed with ease by water.

7-Amino-5-diphenylacridine salts (annexed formula) are obtained



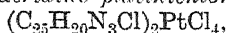
by oxidation of the leuco-compound, 7-amino-5-diphenyldihydroacridine, in acid solution by means of ferric chloride. Other solid salts are difficult to obtain, but the *perchlorate*, $C_{25}H_{19}N_3ClO_4$, forms a pure yellow, pulverulent, crystalline precipitate

exploding when heated.

5-Diphenylacridine, $C_{25}H_{19}N_3$, forms small, pale yellow crystals decomposing without melting at 160° , and acts as a very weak base.

1(or 9):7-Diaminodiphenylacridine hydrochloride, $C_{25}H_{20}N_3Cl$, forms deep, olive-green, crystalline flocks, and the *platinichloride*, $(C_{25}H_{20}N_3Cl)_2PtCl_4$, small, dark green crystals. The *imide* base, $C_{25}H_{18}N_3$, separates, apparently as a hydrate, in deep red flocks, changing in a few minutes to fine crystals.

3:7-Diaminodiphenylacridine platinichloride,



forms metallic-green crystals, somewhat soluble in water to a greenish-blue solution. The *chloride* forms metallic-green crystals with the lustre of brass. The *imide base*, $C_{25}H_{18}N_3$, forms copper-red crystals with a golden lustre, m. p. $240-250^\circ$ (decomp.).

3:7:9-Triaminodiphenylacridine chloride, $C_{25}H_{21}N_4Cl$, forms

compact crystals with a coppery lustre, and the *platinichloride*, microscopic, blackish-violet crystals insoluble in water.

1 : 3 : 7 : 9-*Tetra-aminodiphenylacridine chloride*, $C_{25}H_{29}N_5Cl$, forms needles with a coppery lustre, and the *base*, leaflets with the lustre of bronze.

Hexa-aminodiphenylacridine chloride (formula VI), $C_{25}H_{24}N_7Cl$ forms almost black prisms with a slight metallic lustre. The base exhibits highly basic characters, and was not isolated, as it is not completely liberated from its salts by alkali hydroxide, and even in ethereal solution rapidly absorbs carbon dioxide from the air.

The constitution of these colouring matters is discussed.

T. H. P.

Derivatives of 3:5-Dinitrophenoxazine. EMIL MISSLIN and ADOLF BAU (*Helv. Chim. Acta*, 1919, 2, 285—315).—The objects of this investigation were: (1) to ascertain how far substitution in *o*-aminophenol by the radicles NO_2 , Cl, and $NHAc$ may be carried without preventing the formation of phenoxazines by the action of either picryl chloride or the more readily accessible 2:4:6-trinitroanisole in presence of an alkaline medium, and (2) to determine if in all cases the formation of phenoxazine takes place by way of an intermediate diphenylamine derivative, or if in certain cases the initial formation of a diphenyl ether is to be assumed.

The results obtained show that the action either of 2:4:6-trinitroanisole or of picryl chloride on *o*-aminophenol or its nitro-, chloro-, bromo-, or acetyl-amino-substituted derivatives of the type of picramic acid leads in presence of alkali to the formation of derivatives of 3:5-dinitrophenoxazine, diphenylamine compounds being formed as intermediate products. It is highly probable, also, that other substituted *o*-aminophenols containing the groups named, with the exception of those in which the substitution occurs in the ortho-position to the amino-group, react in the same sense with 2:4:6-trinitroanisole or picryl chloride. When suspended in alcohol, 3:5-dinitrophenoxazines substituted in the 7-position by NO_2 , Cl, Br, or $NHAc$ yield Bordeaux-red or violet colorations on addition of alkali hydroxide, whilst 3:5-dinitrophenoxazines with a nitro-group in the 6-position yield a pure blue coloration under these conditions. With simultaneous substitution in the 6- and 7-positions, the coloration is determined by the more highly negative substituent, or, if the two substituents are of similar character, by that in the 6-position. The condensation product obtained in the cold from picryl chloride and the potassium derivative of *o*-acetylaminophenol yields Turpin's 3:5-dinitrophenoxazine (T., 1891, 59, 714) on treatment with alkali.

3:5-Dinitrophenoxazine, formed from 2:4:6-trinitroanisole and *o*-aminophenol in alcoholic solution in presence of potassium hydroxide, is also obtained from the *p*-toluenesulphonic ester of 2:4:6-trinitro-2'-hydroxydiphenylamine under similar conditions, and from 2:4:6-trinitro-2'-hydroxy-*N*-acetyldiphenylamine by treatment with ammonia in alcoholic solution.

8-Chloro-3:5-dinitrophenoxazine, $C_{12}H_6O_3N_3Cl$, formed either

from 2:4:6-trinitroanisole and 4-chloro-2-aminophenol or from 5'-chloro-2:4:6-trinitro-2'-hydroxydiphenylamine *p*-toluenesulphonate, crystallises in brick-red or deep brownish-red needles. In concentrated sulphuric acid it forms a Bordeaux-red solution, which precipitates it unchanged on dilution; when suspended in alcohol, it yields a pure violet coloration with alkali hydroxide.

3:5:8-*Trinitrophenoxazine*, $C_{12}H_6O_7N_4$, obtained from 2:4:6-nitroanisole and 4-nitro-2-aminophenol, forms deep reddish-brown needles, and gives a Bordeaux-red solution in alkaline alcohol.

3:5-*Dinitro-8-acetylaminophenoxazine*, $C_{14}H_{10}O_6N_4$, prepared from 4-acetylamino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, A., 1902, i, 795), forms dark brown, velvety, felted needles. Its solution in concentrated sulphuric acid is first brownish-red and then dark red, addition of water producing a brownish-yellow precipitate. Its suspension in alcohol is coloured violet by potassium hydroxide.

3:5:9-*Trinitrophenoxazine*, obtained from 2:4:6-trinitroanisole and 5-nitro-2-aminophenol, was prepared by Kehrman and Saager (A., 1903, i, 279) by nitration of 3:5-dinitrophenoxazine.

8-*Chloro-3:5-dinitro-10-aminophenoxazine*, $C_{13}H_7O_5N_4Cl$, obtained from 4-chloro-2:6-diaminophenol and 2:4:6-trinitroanisole, forms slender, reddish-brown, shining needles, gives a yellowish-brown solution in concentrated sulphuric acid, and yields a dull violet coloration with potassium hydroxide in alcohol.

8:10-*Dichloro-3:5-dinitrophenoxazine*, $C_{13}H_5O_5N_3Cl_2$, prepared from 4:6-dichloro-2-aminophenol and 2:4:6-trinitroanisole, forms small, reddish-brown, shining crystals, sparingly soluble in concentrated sulphuric acid, giving a reddish-violet coloration; in alkaline alcohol it forms a violet solution with a red tinge.

8:10-*Dibromo-3:5-dinitrophenoxazine*, $C_{13}H_5O_5N_3Br_2$, prepared like the corresponding dichloro-compound, forms deep reddish-brown, shining needles, and dissolves slightly in concentrated sulphuric acid with a faint blue coloration; with alcoholic alkali, a violet coloration with a red tinge is formed.

8-*Chloro-3:5:10-trinitrophenoxazine*, $C_{13}H_5O_7N_4Cl$, obtained from 2:4:6-trinitroanisole and 4-chloro-6-nitro-2-aminophenol, crystallises in drusy masses of matt, light brown leaflets, and gives a brownish-orange solution in concentrated sulphuric acid; its suspension in alcohol gives a violet coloration with alkali hydroxide.

3:5:8-*Trinitro-10-aminophenoxazine*, $C_{12}H_7O_7N_5$, prepared from 4-nitro-2:6-diaminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), crystallises in shining, reddish-brown to garnet-red needles, and dissolves readily in concentrated sulphuric acid to an intense brownish-yellow solution. In alcoholic potassium hydroxide, it dissolves incompletely to a dirty, brownish-red solution. When boiled with acetic anhydride and fused sodium acetate, it is converted into 3:5:8-*trinitro-10-acetylaminophenoxazine*, $C_{14}H_9O_8N_5$, which may also be obtained from 4-nitro-6-acetylamino-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitrolate (compare Meisenheimer, *loc. cit.*), and which forms brownish-yellow leaflets

with the lustre of gold. It dissolves easily in concentrated sulphuric acid to an orange-yellow solution; and partly in alcoholic alkali hydroxide with a violet coloration showing a red tinge.

10-Chloro-3:5:8-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, prepared from 2:4:6-trinitroanisole and 6-chloro-4-nitro-2-aminophenol, forms drusy masses of small, reddish-brown, shining crystals, and readily gives an orange solution in concentrated sulphuric acid; with alcohol and potassium hydroxide, it gives a reddish-violet to Bordeaux-red solution.

3:5:10-Trinitro-8-acetylaminophenoxazine, $C_{14}H_9O_8N_5$, obtained from 4-acetyl-amino-6-nitro-2-aminophenol and potassium 3:5-dinitro-4:4'-dimethoxyquinolnitate, forms shining, flat, pale reddish-brown needles, and gives a brownish-orange solution in concentrated sulphuric acid and a violet coloration with alkali hydroxide in suspension in alcohol.

8-Chloro-3:5:9-trinitrophenoxazine, $C_{12}H_5O_7N_4Cl$, obtained either from 2:4:6-trinitroanisole and 4-chloro-5-nitro-2-aminophenol or by nitration of 8-chloro-3:5-dinitrophenoxazine, crystallises in stellar aggregates of shining, garnet-red needles, and gives a dirty, bluish-red solution in concentrated sulphuric acid and a pure blue coloration with alkali hydroxide and alcohol.

3:5:7:9-Tetranitrophenoxazine, obtained by nitration of 3:5:9-trinitrophenoxazine, agrees in properties with Kehrmann and Saager's preparation (*loc. cit.*).

3:5:9-Trinitro-8-methylphenoxazine, $C_{13}H_8O_7N_4$, prepared from 2:4:6-trinitroanisole and 5-nitro-2-amino-*p*-cresol, forms deep reddish-brown, shining needles, and readily dissolves in concentrated sulphuric acid to a dirty, brownish-red solution; a pure blue solution is obtained in alcohol and potassium hydroxide.

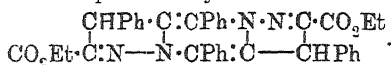
3:5:8:10-Tetranitrophenoxazine, $C_{12}H_5O_9N_5$, prepared from picramic acid and either 2:4:6-trinitroanisole or picryl chloride, forms dark brown or steel-blue needles, and yields an intensely golden-yellow solution in concentrated sulphuric acid and a bluish-red solution in alcoholic alkali hydroxide.

3:5:8:9-Tetranitrophenoxazine, $C_{12}H_5O_9N_5$, prepared by nitrating 3:5:8-trinitrophenoxazine, forms long, reddish-brown leaflets with a green, metallic lustre, containing acetic acid of crystallisation, and assumes an orange-red colour when dried. It dissolves easily in concentrated sulphuric acid with an orange-red coloration, and in alcohol containing alkali hydroxide to a greenish-blue solution.

T. H. P.

Coloured Condensation Products from Ketonic Pyrazoline Derivatives. E. P. KOHLER and L. L. STEELE (*J. Amer. Chem. Soc.*, 1919, **41**, 1105—1108).—The ketopyrazolines having the structure $-CO \cdot CH < \text{NH}-$ give highly fluorescent solutions in alcohol containing a trace of hydrogen chloride. Some of the products have now been isolated. They are very sparingly soluble substances of high m. p. and molecular weight, and outwardly resemble the most brilliant rhodamine dyes.

Hydrogen chloride is passed into a suspension of ethyl 5-benzoyl-4-phenylpyrazoline-3-carboxylate (this vol., i., 531) in boiling methyl alcohol, and the crimson precipitate is collected as soon as the ester has disappeared and boiled for some time with carbon disulphide. The compound, $C_{38}H_{32}O_4N_4$, is thereby changed into a mass of stout needles, m. p. 266—268°, which sublime freely at above 400° in a vacuum. It is very slightly soluble in benzene, the solution appearing a brilliant crimson-orange by reflected light and purple by transmitted light. On continuing the action of hydrogen chloride, the substance takes up water and the acid to form a yellow compound, $C_{38}H_{35}O_5N_4Cl$, plates, m. p. 258—259°, and when-boiled with acetic acid for some time it combines with $2H_2O$ to give the colourless compound, $C_{38}H_{36}O_6N_4$, needles, m. p. 181°. From an approximate determination of its molecular weight, it appears that the compound may have the formula



Ethyl 5-*p*-bromobenzoyl-4-phenylpyrazoline-3-carboxylate (*ibid.*) gives a similar product, $C_{38}H_{31}O_4N_4Br$, purple-red needles, m. p. 268—270°.

Distyryl ketone reacts with ethyl diazoacetate in light petroleum at 50—70° to give ethyl 5-cinnamoyl-4-phenylpyrazoline-3-carboxylate, $\text{CHPh} : \text{CH} \cdot \text{CO} \cdot \text{CH} < \begin{array}{c} \text{CHPh} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{NH} - \text{N} \end{array}$, pale yellow plates,

m. p. 164.5—165°, solutions of which become blood-red with hydrogen chloride. Styryl methyl ketone yields ethyl 5-acetyl-4-phenylpyrazoline-3-carboxylate, white needles, m. p. 127°, solutions of which give an orange colour with hydrochloric acid.

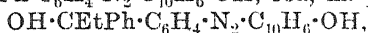
Ethyl 5-acetyl-4-phenylpyrazoline-3:5-dicarboxylate, m. p. 76°, was obtained by Buchner. The present authors have obtained an isomeride with m. p. 105—106°. This gives no colour with alcoholic hydrogen chloride. J. C. W.

Asymmetric Dyes. C. W. PORTER and C. T. HIRST (*J. Amer. Chem. Soc.*, 1919, **41**, 1264—1267).—A number of dyes containing an asymmetric carbon atom have been prepared with the idea of contributing to the knowledge of vital stains, and one has been discovered on which wool acts selectively, absorbing more of the *laevo*- than the *dextro*-modification.

The parent substance is *p*-aminobenzophenone, obtained by condensing benzoyl chloride with phthalanilide in the presence of zinc chloride. This is converted into *p*-aminobenzhydrol by reduction, and into carbinols by the Grignard reaction, and these bases, containing an asymmetric carbon atom, are diazotised and coupled with (a) β -naphthol, giving dyes which are insoluble in acids, alkalis, or water, (b) dimethylaniline in the presence of about 0.1*N*-hydrochloric acid, and (c) naphtholsulphonic acids and naphthylaminesulphonic acids, to give soluble dyes.

p-Aminodiphenylmethylcarbinol, $\text{OH} \cdot \text{CMePh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, has m. p. 101°, and *p*-aminodiphenylethylcarbinol forms colourless

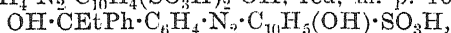
plates, m. p. 103°. The *dyes* mentioned in tabular form in the original are as follows: $\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, red, m. p. 169.5°; $\text{OH} \cdot \text{CMePh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$, red, m. p. 190°;



crimson, m. p. 149°; $\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, red, m. p. 145°; $\text{OH} \cdot \text{CMePh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, yellow, m. p. 177°;

$\text{OH} \cdot \text{CEtPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$, orange, m. p. 138—139°;

$\text{OH} \cdot \text{CHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_4(\text{SO}_3\text{H})_2 \cdot \text{OH}$, red, m. p. 162°;



dark red, m. p. 120—122°; $\text{OH} \cdot \text{CMePh} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{SO}_3\text{H}$, red, m. p. 150—152°. J. C. W.

The Constitution of Internal Diazo-oxides (Diazo-phenols).

II. GILBERT T. MORGAN and ERIC DODDRELL EVANS (T., 1919, 115, 1126—1140).

Action of Phenylhydrazine on Phthalaldehydic and Phthalonic Acids: Phenyl-hydrazo- and Azo-phthalide. PRAFULLA CHANDRA MITTER and JNANENDRA NATH SEN (T., 1919, 115, 1145—1148).

Researches on Proteins. VI. The Destructive Distillation of Fibroin. TREAT B. JOHNSON and PETER G. DASCHAVSKY (*J. Amer. Chem. Soc.*, 1919, 41, 1147—1149).—Like Pictet and Cramer (this vol., i, 227), the authors have also commenced a study of the destructive distillation of proteins, choosing in the first instance silk fibroin, because it contains no sulphur and because its chief amino-acids are well known and few in number (glycine 33%, alanine 16%, and tyrosine 10%). Distilling quantities of about 1600 grams at a time, under 25—27 mm., the authors obtain about 16% of volatile and gaseous products, soluble in sodium hydroxide or sulphuric acid, 41% of coke, and 43% of a red oil which certainly contains phenol. J. C. W.

Application of the Kjeldahl Method to Compounds of Brucine, with Reference to the Brucine Salt of a New Nucleotide. WALTER JONES (*J. Pharm. Exp. Ther.*, 1919, 14, 489—493).—The Kjeldahl method gives exact results with salts of brucine. This fact has been applied in determining the nature of the brucine salt of a nucleotide obtained by partial oxidation of yeast-nucleic acid with potassium permanganate. J. C. D.

Action of Enzymes on Starches of Different Origin. H. C. SHERMAN, FLORENCE WALKER, and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1919, 41, 1123—1129).—When purified by washing with very dilute sodium hydroxide, wheat, rice, and maize starches are hydrolysable at the same rate by the same kind of amylase, and this is true for a large variety of agents, such as saliva, pancreatin, purified pancreatic amylase, malt extract, purified malt amylase, taka-diaxase, or the purified amylase of *Aspergillus oryzae*. When washed with water only, potato starch

is almost pure, but the cereal starches, especially maize starch, appear to contain fatty or resinous substances which interfere with the hydrolysis, even after the starch has been dissolved in boiling water. These interfering substances are partly removed by ether, but best by dilute alkali hydroxide. Potato starch is slightly more digestible than the purified cereal starches. In one case, however, when purified potato starch was left with purified pancreatic amylase, a much lower rate of hydrolysis was observed, suggesting that some accessory substance had been removed during the purification.

The experiments on which these conclusions are based were carried out as follows. Sufficient of the starch preparations were taken to furnish 1% solutions of real, dry starch, and gelatinised by boiling with water for three minutes. The solutions were then rendered neutral to rosolic acid and made up to 100 c.c. at 40° in a thermostat. Uniform volumes of the enzyme preparations, sufficient to cause hydrolysis to proceed to about one half, were then placed with any necessary salts in several flasks and the starch solutions added. After thirty minutes at 40°, the hydrolysis was stopped by rapidly boiling the mixture, and the reducing sugar was estimated by Fehling's method.

J. C. W.

The Action of Ptyalin. HUGH MCGUIGAN (*J. Biol. Chem.*, 1919, **39**, 273—284).—Chittenden and Smith (*T. Conn. Acad. Arts and Sci.*, 1885, **6**, 343) studied the action of ptyalin on starch and found that a relation between the amount of sugar formed and the amount of ptyalin used existed only when the saliva was diluted 50 to 100 times. These experiments have been in the main confirmed by the author, who has also found that the balance point shifts with the volume of saliva used, and that it may go as high as 75% of the substrate—calculated as dextrose. The products of digestion which interfere with the reaction are not dextrose or maltose. There is evidence that ptyalin combines with starch during digestion, and exerts a force which causes hydrolysis.

J. C. D.

Arsenical Medical Product and Process of Producing Same. J. M. WHITE (U.S. Pat. 1297952).—A product believed to be sodium dimethylphenyl hydrogen arsenide, $C_6H_5Me_2 \cdot AsHNa$, m. p. about 121°, readily soluble in water, is obtained by the interaction of sodium benzoate and sodium cacodylate in aqueous solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 847A.]

Physiological Chemistry.

Concentration of Ammonia in Blood. Comparison with Concentration of Ammonia in Different Secretions and Tissues, especially Muscle Tissue. K. L. GAD-ANDERSEN (*J. Biol. Chem.*, 1919, **39**, 267—271).—A method for the estimation of ammonia in the tissues is described. The author records that he found the concentrations of ammonia in muscle and in blood of the same order. The concentration of ammonia in the heart muscle, liver, fatty tissue, bile, cerebro-spinal fluid, and aqueous humour is the same as in blood. J. C. D.

Some Data concerning the Alleged Relation of Catalase to Animal Oxidations. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1919, **39**, 403—420).—The feeding of meat and the administration of "saccharin," β -hydroxybutyric acid, alanine, and glycine are not accompanied by an increase in the catalase content of the blood to the extent reported by Burge (*Amer. J. Physiol.*, 1918, **46**, 117; 1918—1919, **47**, 13). It is suggested that fluctuations in catalase content are due to fluctuations in the red cell count of the blood, and that catalase content is a function of the number of red cells. J. C. D.

Importance of Accurate and Quantitative Measurements in Experimental Work on Nutrition and Accessory Food Factors. HARRIETTE CHICK and E. MARGARET HUNE (*J. Biol. Chem.*, 1919, **39**, 203—207).—The authors point out that much of the experimental work recently published on the subject of the accessory food factors may be criticised on the ground that quantitative measurements have not received sufficient attention. In comparing the value of a series of foodstuffs as regards their value in content of some accessory food factors, it is obvious that the first step necessary is to determine in each case the minimum daily dose which will maintain health in the experimental animal, and to institute comparison between these amounts.

Neglect of this necessary procedure has led to many vague and erroneous results being reported. J. C. D.

Hydrogen- and Hydroxyl-ion Equilibrium in Solutions. I. W. LÖFFLER and K. SPIRO (*Helv. Chim. Acta*, 1919, **2**, 417—419).—Most of the liquids of the animal organism exhibit the same reaction approximating to neutrality, the maintenance of this reaction being of the utmost importance for many physiological processes, and alterations in it being of great influence on the course of essential vital processes. In an investigation of the extent to which the results obtained with colloidal solutions are applicable to solutions of crystalloids, the authors have attained a simple demonstration of the fact that the neutrality of crystalloid solu-

tions is regulated by physico-chemical as well as by chemical factors. In all adsorption processes, specific forces act, different substances showing considerable differences as regards adsorbability. Alteration of the reaction by shaking with animal charcoal is not shown by all solutions used as "moderators" or "buffers"; thus, no such change occurs with phosphate solutions, whereas with solutions of citrates and borates it is easily detectable, the value of p_H being increased with the former and diminished with the latter salts. The use to which animal charcoal is now put in the treatment of infective diseases may depend, not merely on its ability to absorb bacteria and toxins, but also on its action in combating the acidity of the stomach contents arising from bacterial influence. T. H. P.

Equilibrium between Potassium, Rubidium, Cæsium, and Uranium. (MLE.) L. KAISER (*Arch. Néerland Physiol.*, 1919, 3, 587—593).—Potassium in Ringer's solution may be replaced by rubidium or cæsium, as far as its action on the isolated frog's heart is concerned. The maximum action is given by the following concentrations, expressed as mg. per litre: potassium 92, rubidium 116, cæsium 78. It has been shown that certain elements, such as uranium, thorium, and radium, which should be capable of replacing potassium, actually exert an opposite effect. This is viewed in the light of the fact that potassium emits negative β -rays, whilst uranium emits positive α -rays. The antagonistic action of these elements on the frog's heart is considered.

J. C. D.

Composition of the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. McARTHUR (*J. Amer. Chem. Soc.*, 1919 41, 1225—1240).—See this vol., ii, 483.

The Supposed Occurrence of Methylguanidine in Meat, with Observations on the Oxidation of Creatine by Mercuric Acetate. ISIDOR GREENWALD (*J. Amer. Chem. Soc.*, 1919, 41, 1109—1115).—Most of the reports that methylguanidine occurs in meat are based on the use of either silver nitrate and barium hydroxide or mercuric chloride and sodium acetate as the precipitating agents. Ewins has already shown that the former agent is capable of oxidising creatine to methylguanidine (*A.*, 1916, i, 528), and it is now proved that mercuric acetate is equally unsatisfactory, for not only does it fail to give complete precipitation, but it also oxidises creatine to methylguanidine and oxalic acid, and an intermediate product, methylguanidoglyoxylic acid, $NHMe \cdot C(NH) \cdot NH \cdot CO \cdot CO_2H$. These results have recently been confirmed by Baummann and Ingvaldsen (*A.*, 1918, i, 423).

Using a modification of the process by which Brieger isolated methylguanidine from very putrid meat in connexion with his work on ptomaines, the author has failed to find any of the base in fairly fresh meat.

J. C. W.

Metabolism of Dextrose in Surviving Organs. VII. Action of Muscular Tissue of the Dog (during Feeding and Fasting) on Dextrose Circulating in it and on the Glycogen contained in it. UGO LOMBROSO and LUDOVICO PATERNI (*Arch. farm. sper. sci. aff.*, 1919, 27, 17—32).—When placed under suitable conditions, the muscular tissue of the dog is able to consume, not merely its own glycogen, but also marked quantities of dextrose added to the liquid circulating through it, such consumption being the greater when the tissue is from a dog being fed than when it is from one kept fasting. T. H. P.

The Salicylates. XI. The Stability and Destruction of the Salicyl Group under Biological Conditions. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, 14, 25—42).—It has been previously reported that 20 to 30% of the salicyl group remains unaccounted for after its passage through the body, and is presumably destroyed (*ibid.*, 1917, 9, 247). Solutions of sodium salicylate deteriorate when kept, particularly when they are dilute. The decomposition appears to be due to the action of living organisms, and may be inhibited by adding chloroform. Sodium salicylate solutions were found to deteriorate in the presence of yeast, but not as rapidly as when allowed to remain alone. The salicyl group appears to undergo destruction when in the presence of minced tissue. About 20% of salicylates administered to normal individuals is destroyed, whilst in the cat and dog the amount destroyed is much greater.

A general increase in metabolism, such as is encountered in febrile conditions, leads to an increased destruction of the salicyl group. J. C. D.

The Salicylates. XII. The Excretion of Salicyl after Administration of Methyl Salicylate to Animals. P. J. HANZLIK and N. C. WETZEL (*J. Pharm. Exp. Ther.*, 1919, 14, 43—46).—The excretion of salicyl by animals (dogs and cats) after the administration of methyl salicylate is approximately 25% less than after the administration of sodium salicylate. After gastric administration, the free ester was found in the urine in concentrations of 0.2 to 0.52%, and 14.4% after intramuscular injection. J. C. D.

Chemistry of Vegetable Physiology and Agriculture

Mineral Matter in Plants: The Ashes of some Roots and Tubers. LUCIEN LEROUX and DÉSIRÉ LEROUX (*Ann. Chim. anal.*, 1919, [ii], 1, 207—209).—The following amounts of ash were found in the air-dried substances: Potato, 4.05%; common comfrey, 9.06%; dahlia, 5.10%; burdock, 12.25%; thistle, 11.45%; gentian,

3.65%; carrot, 6.25%; turnip, 7.15%; water lily, 3.65%; nettle, 7.83%; male fern, 4.83%. Analyses of the ashes are also given. The largest quantities of sulphuric acid were found in thistle ash and turnip ash (18.5% and 13.2% of SO_3 respectively); phosphoric acid was most abundant in water-lily ash (14.7% P_2O_5), and calcium in gentian ash (19.0% CaO). Gentian ash also yielded the largest quantity of iron, namely, 6.3% Fe_2O_3 . W. P. S.

Carbohydrates of Vegetables. V. Carbohydrates of Carrots. VI. Carbohydrates of Green Peas. ERNST BUSOLT (*J. Landw.*, 1916, **64**, 357—360, 361—362. Compare A., 1914, i, 792).—Carrots (6 kilos. of fresh roots) contain mannitol (23.5 grams) and dextrose (2.8 grams), whilst green peas contain mannitol, dextrose, levulose, and glycuronic acid. T. H. P.

Secretion of Phosphates in the Stems of Djatikapur [*Tectona grandis*, L.]. A. WICHMANN (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 968—982).—A discussion on the nature of the mineral deposits found in the stems of teak trees. From a consideration of the data the author concludes that the deposits are hydrated calcium phosphate, and that this may change into calcium magnesium phosphate. The teak tree absorbs more phosphoric acid than any other tree, and the effects of this on the nature of the soil are considered. J. F. S.

Content of Hydrastine and Berberine in *Hydrastis canadensis* Grown in Austria (at Korneuberg) and Estimation of Berberine. RICHARD WASICKY and MARIANNE JOACHIMOWITZ (*Arch. Pharm.*, 1917, **255**, 497—506).—An accurate method for estimating berberine is described, and also the results of the estimation of hydrastine and berberine in the different parts of *Hydrastis canadensis* grown in Austria. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

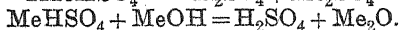
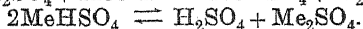
The Action of some Common Soil Amendments. J. E. GREAVES and E. G. CARTER (*Soil Sci.*, 1919, **7**, 121—160).—From a review of the literature on this subject, a full bibliography of which is given, it is shown that the sulphates of magnesium, calcium, and iron, the chlorides of sodium, potassium, magnesium, and calcium, and manganese and iron salts may be especially efficient as soil stimulants. This effect is due in some cases to an increase in the available phosphate, and in others to an increase in the available nitrogen, these increases in available nitrogen and phosphorus being quite sufficient to account for the noted increase in crop yields resulting from the use of these soil amendments. In certain cases, an increase in the organic phosphorus rather than in the available phosphate or nitrogen results from their application. W. G.

Organic Chemistry.

Chlorination of Methane. J. PFEIFER, F. MAUTHNER, and O. REITLINGER (*J. pr. Chem.*, 1919, [ii], **99**, 239—242).—The process has been studied by passing suitable mixtures of chlorine and a natural gas consisting of nearly pure methane, free from ethylene hydrocarbons but containing small amounts of nitrogen and oxygen, over antimony pentachloride or ferric chloride contained in a quartz tube heated at 360—400°. With the former catalyst and the gases mixed in the proportion of one volume of methane to two volumes of chlorine, methylene chloride (5·8%), chloroform (20·3%), carbon tetrachloride (5·9%), and hydrogen chloride (32%) were obtained, 64% of the chlorine entering into action. With ferric chloride and equal volumes of the two gases, the substances formed were methyl chloride (5·8%), methylene chloride (15·7%), chloroform (21·7%), and hydrogen chloride (43·2%), 86·4% of the chlorine being used; when 2 volumes of chlorine were employed for each volume of methane, there were obtained methyl chloride (traces), methylene chloride (13·25%), chloroform (22·2%), carbon tetrachloride (6·35%), and hydrogen chloride (41·8%), 83·6% of the chlorine entering into action. With 2 volumes of methane to 1 volume of chlorine, 30·1% of methyl chloride and a mixture of approximately equal amounts of methylene chloride and chloroform were produced. When the proportion of methane to chlorine was 3:1, the yield of methyl chloride rose to 40% of that theoretically possible. Attempts to secure carbon tetrachloride in good yield by increasing the relative amount of chlorine were rendered difficult by the occurrence of violent explosions; a mixture of chloroform and carbon tetrachloride was, however, obtained by the use of methane (1 vol.) and chlorine (3 vols.) diluted with nitrogen (2 vols.).

H. W.

Action of Concentrated Sulphuric Acid on Methyl Alcohol. J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, **169**, 655—657).—The yield of methyl sulphate in the action of sulphuric acid on methyl alcohol increases steadily as the molecular proportion of the sulphuric acid in the reacting mixture increases. The complete mechanism of the reaction is given by the three equations:



The combined equilibrium of the first two reactions is, to a large extent, independent of the temperature, but the velocity with which the equilibrium is reached is largely influenced by the temperature.

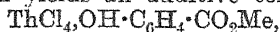
W. G.

Action of Sulphuric Anhydride and of Fuming Sulphuric Acid on Methyl Alcohol. Preparation of Methyl Sulphate.

J. GUYOT and L. J. SIMON (*Compt. rend.*, 1919, 164, 795—797).—By the action of 60% fuming sulphuric acid on pure methyl alcohol in the calculated proportion, methyl sulphate may readily be obtained, the yield exceeding 90%. An alternative method is to pass the vapour of methyl ether into the acid until the whole of the sulphuric anhydride, which it contains, is converted into methyl sulphate, and then to distil the mixture. [See, further, *J. Soc. Chem. Ind.*, 1919, 924A.] W. G.

Compounds of Thorium. I. Addition and Substitution Compounds of Thorium Chloride. G. JANTSCH and W. URBACH

(*Helv. Chim. Acta*, 1919, 2, 490—500).—Thorium chloride on boiling with absolute alcohol forms a white, very deliquescent additive compound, $\text{ThCl}_4 \cdot 4\text{EtOH}$; this crystallises in fine, prismatic plates, and slowly loses alcohol on keeping. On shaking anhydrous thorium chloride with acetone, solution occurs after a short time, and on keeping over phosphoric oxide the additive compound, $\text{ThCl}_4 \cdot 2\text{C}_6\text{H}_5\text{O}$, separates in small, white, prismatic needles. Heating thorium chloride with acetophenone in chloroform solution gives a clear solution which on keeping over phosphoric oxide yields long, white needles of $\text{ThCl}_4 \cdot 4\text{C}_6\text{H}_5\text{O}$, which are very hygroscopic and lose the whole of their acetophenone on keeping. A similar compound, $\text{ThCl}_4 \cdot 4\text{C}_6\text{H}_4\text{O}$, is produced when benzophenone is substituted for acetophenone in the last preparation. Thorium acetate is prepared as a white, crystalline mass by heating anhydrous thorium chloride with anhydrous acetic acid. Thorium benzoate is prepared as a white, crystalline precipitate by heating benzoic acid in xylene solution with anhydrous thorium chloride as long as hydrogen chloride is evolved. If, however, the reaction takes place in light petroleum of high boiling point the chlorobenzoate is produced. This compound, $\text{ThCl}_4 \cdot (\text{OBz})_3$, is very hygroscopic, and is quite insoluble in benzene and chloroform. When thorium chloride is heated with four molecules of salicylaldehyde in ethereal solution a clear, yellow solution is produced, from which on further heating separates a light yellow, crystalline, additive compound, $\text{ThCl}_4 \cdot 2\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$. If, however, the ether is replaced by chloroform, the substitution product, $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2$, is formed as a canary-yellow, crystalline precipitate, which is very hygroscopic. Thorium chloride heated with three molecules of methyl salicylate in ethereal suspension yields an additive compound,



in fine, white needles; if chloroform, benzene, or xylene is substituted for ether, three substitution products are obtained, depending on the amount of ester employed, (1) with 2 molecules of ester in chloroform the compound $\text{ThCl}_3 \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$ is formed in fine, white needles; (2) with 4 molecules of ester in benzene the compound $\text{ThCl}_2(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_2$ is formed in white needles; (3) with 6 molecules of ester in xylene a faintly yellow substance,

$\text{ThCl}(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me})_3$, is obtained, which on washing with light petroleum becomes white. J. F. S.

Ethylene Chlorohydrin and $\beta\beta'$ -Dichloroethyl Sulphide. M. GOMBERG (*J. Amer. Chem. Soc.*, 1919, **41**, 1414—1431).—An account of work done under the auspices of the American Bureau of Mines, War Gas Investigations. Many of the conclusions are already well known, but they may be summarised as follows.

I. *Preparation of Ethylene Chlorohydrin.*—In analogy to the reactions between bromine water and ethylene discussed by Read and Williams (T., 1917, 111, 240), the author expected that the controlling factors would be the velocities of the reactions between ethylene and chlorine or hypochlorous acid, and actually found that by passing the two gases into water, keeping ethylene in slight excess, a concentration of 6—8% of chlorohydrin is reached before an appreciable amount of dichloride is formed. Up to this point the gases are absorbed rapidly at 10—12° (about 20—25 litres of each per hour in the experiments), but thereafter the reaction becomes sluggish. With a slow stream of gas, however, concentrations of chlorohydrin as high as 14—15% may be reached, but always accompanied by much dichloride. The influence of dissolved chlorohydrin, hydrogen chloride, or metallic chlorides on the course of the reaction was roughly determined. Chlorohydrin itself is rather helpful at the outset, and hydrochloric acid up to 2*N* is no hindrance to the exclusive production of the chlorohydrin. The combined effect, however, is more important, for when both are present in *N*-concentration, the formation of ethylene dichloride is favoured. Metallic salts are much more harmful, and consequently any attempt to neutralise the hydrochloric acid formed during the reaction $[\text{H}_2\text{O} + \text{Cl}_2 \rightleftharpoons \text{HClO} + \text{HCl}]$ does more harm than good. Efficient stirring is obviously most important. Altogether, it is not advisable to aim at more than 8% concentrations of chlorohydrin. The refractive index gives a measure of the concentration (water, 1.333; chlorohydrin, 1.442).

II. *Concentration and Isolation of the Chlorohydrin.*—A 42.5% solution of chlorohydrin in water has the constant boiling point 95.8°. More dilute solutions can therefore be enriched by distillation, and entirely freed from hydrochloric acid. The effect of salts on the course of the distillation is striking. For example, 9 litres of a 7.3% solution were neutralised with lime and distilled, 4 litres being collected; this was saturated with salt and distilled again, 1.6 litres being collected; this was saturated with calcium chloride and concentrated by distillation to 1 litre, the resulting solution containing nearly all the original chlorohydrin, being 64%. The subject of "salting out" the chlorohydrin appears to offer many interesting problems. Saturation with sodium sulphate* at 32—33° seems to offer the best results; the aqueous layer is about 7% chlorohydrin, whilst the separated oil contains about 68% of chlorohydrin and only about 0.65 gram of sodium sulphate per 100 c.c. A combination of distillation, "salting out," and extraction with ether, benzene, or perhaps ethylene dichloride would be the best scheme

for isolating the pure compound. Very little hydrolysis takes place during the distillations.

III. *Conversion into $\beta\beta'$ -Dichloroethyl Sulphide.*—The reaction with sodium sulphide proceeds just as well with 20% solutions of chlorohydrin as with more concentrated solutions, and only a small excess of the salt is required. Concentration being necessary at some point, however, it is best to use 40—80% solutions. After the reaction, which is completed by warming, the solution is neutralised by sulphuric acid and evaporated under reduced pressure, when the thiodiglycol, $S(CH_2 \cdot CH_2 \cdot OH)_2$, may be extracted by alcohol. If the isolation of this is not required, however, 70—80% chlorohydrin is added to solid sodium sulphide, the product is neutralised by 90% sulphuric acid, and then mixed with concentrated hydrochloric acid. The salts are filtered and the solution warmed at 60—75°, when the "mustard gas" separates as an oil almost dry and free from hydrogen chloride, the yield being 90—98%.

In an attempt to prepare $\beta\beta'$ -dichloroethyl sulphide by the interaction of ethylene dichloride and metallic sulphides, it was soon realised that the desired product was more reactive than the parent substance, a disulphide, $(C_2H_4)_2S_2$, being formed when "mustard gas" is even left with sodium sulphide solution in the cold.

J. C. W.

Superpalite [Trichloromethyl Chloroformate]. H. P. HOOD and H. R. MURDOCK (*J. Physical Chem.*, 1919, **23**, 498—512).—The preparation, properties, and decomposition of trichloromethyl chloroformate have been studied. The best method of preparation consists in treating methyl alcohol with carbonyl chloride and chlorinating the product, methyl chloroformate, in bright light with elevation of temperature as the chlorination proceeds. Attempts to prepare this compound directly from carbonyl chloride, or from carbon dioxide and carbon tetrachloride, failed. Trichloromethyl chloroformate is decomposed by charcoal and by ferric oxide into carbonyl chloride. When working in sealed tubes at constant temperature the reaction can be brought to a standstill at any desired point in the presence of iron oxide. Alumina decomposes superpalite into carbon tetrachloride and carbon dioxide. Perchlorodimethyl carbonate breaks up on heating into superpalite and carbonyl chloride. When methyl chloroformate is chlorinated in light at suitable temperatures the products are chloromethyl chloroformate (b. p. 107°), dichloromethyl chloroformate (b. p. 114°), and trichloromethyl chloroformate (b. p. 128°). When methyl carbonate is chlorinated, the successive products are monochloromethyl carbonate, b. p. 138°, dichloromethyl carbonate, b. p. 178°, and hexachloromethyl carbonate, m. p. 78°. J. F. S.

The Catalytic Reduction of Halogenated Acetic Esters. PAUL SABATIER and A. MAILHE (*Compt. rend.*, 1919, **169**, 758—761).—The halogenated acetic esters may readily be reduced to the corresponding acetic esters by passing their vapours along with hydrogen over reduced nickel at 300°. This method has been

successfully applied to ethyl mono-, di-, and tri-chloroacetates and ethyl bromoacetate, good yields of ethyl acetate being obtained. In the case of the di- and tri-chloroacetates, the removal of the chlorine takes place in successive stages. In each case small amounts of ethylene and acetaldehyde are obtained, due to secondary decomposition of the ethyl acetate.

W. G.

[Preparation of] Acetic Anhydride and Paracetaldehyde from Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat. 1306963).—A mixture of ethylidene diacetate (400 parts) with sulphuric acid (D 1.87) (8 parts) is heated at 70–80° at a pressure of about 100 mm. In two hours 350 parts of a mixture of paracetaldehyde and acetic anhydride distil, and a residue comprising sulphuric acid and 50 parts of unchanged ethylidene diacetate remains in the reaction vessel. To this 350 parts of ethylidene diacetate may then be added and the reaction continued as before. Distillation is facilitated by passing a current of pure or diluted oxygen into the mixture. The formation of the tarry by-products obtained when higher temperatures are employed in effecting the operation at atmospheric pressure is prevented by conducting the reaction in a vacuum.

CHEMICAL ABSTRACTS.

[Preparation of] Ethylidene Diacetate. J. KOETSCHET and M. BEUDET (U.S. Pat., 1306964).—Mercuric oxide (40 parts) is dissolved in acetic acid (800 parts), the temperature raised to 70°, and a hot solution of β -naphthalenesulphonic acid in acetic acid (200 parts) is added slowly with stirring. A white precipitate of mercuric naphthalenesulphonate is formed. Acetylene is passed into this mixture at 70°, 200 parts being absorbed during two hours. The ethylidene diacetate formed is then separated from the excess of acetic acid. According to a modification of the procedure, mercuric oxide (40 parts) is dissolved in glacial acetic acid (1000 parts) heated at 70°, and into this solution is run a mixture of sulphoacetic acid (26 parts) and acetic acid (100 parts). On passing acetylene into the resulting mixture, 230 parts of acetylene are absorbed in five hours at 65°. The use of mercuric acetate together with aromatic or aliphatic sulphonic acids, instead of mercuric sulphate, as catalyst enables the reaction to be carried out at lower temperatures without deposition of tarry by-products such as are produced when mercuric sulphate is used and the reaction is effected at 90°.

CHEMICAL ABSTRACTS.

The Distillation of Sodium Stearate and Oleate under Reduced Pressure, and the Origin of Petroleum. AMÉ PICTET and JACQUES POTOK (*Helv. Chim. Acta*, 1919, 2, 501–510).—By the distillation of one kilo. of sodium stearate in ten portions, under 12–15 mm., 700 grams of a pasty mass of hydrocarbons are obtained, leaving 200 grams of a residue which contains very little carbon, or salts of the lower fatty acids, being almost entirely sodium carbonate. The distillate consists chiefly of decane, b. p. 172–175°, tetradecane, b. p. 235–238°, pentadecane, b. p.

257—260°, with tetratriacontane, b. p. above 360°, m. p. 73.5°, as the main constituent, and obviously the primary product. No unsaturated or cyclic hydrocarbons are present. The physical properties of the four hydrocarbons agree with the data assigned by Mabery to specimens isolated from Pennsylvanian petroleum. Dry sodium oleate also gives a 70% yield of oil under these conditions, but all the fractions are ethylenic. The chief hydrocarbons found are nonylene, b. p. 145—148°, decylene, b. p. 160—163°, D_4^{20} 0.7630, n_D^{20} 1.4301, undecylene, b. p. 195—198°, and tridecylene, b. p. 228—231°, agreeing in physical properties with the olefines isolated by Coates and Mabery from American petroleum. No naphthenes are present.

The results therefore confirm Engler's hypothesis, in so far as the open-chain hydrocarbons are concerned, namely, that they originate from the fats of marine plants and animals. As the conditions of the decompositions now effected are about as mild as they could very well be, the absence of any traces of cyclic hydrocarbons, especially optically active naphthenes, would strongly suggest a totally different origin for such substances in natural petroleum, and the authors regard the resins and terpenes as the source.

J. C. W.

The Direct Replacement of Glycerol in Fats by Higher Polyhydric Alcohols. I. Interaction of Olein and Stearin with Mannitol. ARTHUR LAPWORTH and LEONORE KLETZ PEARSON (*Biochem. J.*, 1919, 13, 296—300).—Glycerol can be quantitatively replaced by mannitol in fats by heating the fat with mannitol in the presence of sodium ethoxide under reduced pressure. An almost theoretical yield of glycerol is obtained in the distillate, whilst the residue in the distillation flask may be treated so as to obtain a synthetic mannitol fat. The maximum yield of glycerol is obtained when the proportion is two molecules of fat to three of mannitol. The mannitol compounds formed appear to be mixtures of di-oleates (or di-stearates) of mannitan or isomannide.

J. C. D.

The Walden Inversion. P. KARRER and W. KAASE (*Helv. Chim. Acta*, 1919, 2, 436—454).—Various reactions in the glutaric acid series have been studied, with particular reference to the measurement of the rotations of the products for light of different wave-lengths, from about 656 μ to 461 μ . When the rotations for sodium light only are examined, a fairly regular, but meaningless, fluctuation from *d*- to *l*- is observed, but when the rotation-dispersion curves are considered, a completely different conception of the changes may be formed. Thus, of all the following compounds, formed in the order named, and given the sign of rotation for sodium light, namely, *d*-glutamic acid, *l*- α -chloroglutaric acid, zinc *d*- α -hydroxyglutarate, *l*- α -hydroxyglutaric acid, *d*-butyrolactone- γ -carboxylic acid, and also the ethyl *l*-pyroglutamate formed from the initial acid and the *d*-silver salt of the butyrolactone- γ -carboxylic acid obtained from the *l*-chloroglutaric acid, the only product which gives higher negative rotations the shorter the wave-length,

is the α -chloroglutaric acid. All the others give rotation-dispersion curves which tend to rise to highest points in the positive field. It appears, therefore, that only in the replacements of the amino-group by halogen, and this by hydroxyl, are there any changes in configuration, which is, of course, plausible, for these are the only changes directly affecting the asymmetric carbon atom. The authors go so far as to suggest that the symbol d - should be given to those compounds which tend to give positive maxima for their rotations, and l - to those which give negative maxima.

To a certain extent, the results and views expressed agree with those of Clough (T., 1918, 113, 526). In one particular, however, there is contradiction. Clough states that phosphorus pentachloride and thionyl chloride produce from α -hydroxy-aliphatic acids chloro-acids of the same configuration, whereas nitrosyl chloride acting on α -amino-acids gives chloro-acids of opposite sign, and the exchange of halogen by hydroxyl, with silver oxide, is accompanied by another change of sign. If both statements are true, a l -chloro-acid should give a d -hydroxy-acid, and this a d -chloro-acid, but in the present case it is found that l - α -chloroglutaric acid may be converted into the d -hydroxy-acid and this reconverted into the l - α -chloro-acid by phosphorus pentachloride.

Similar regularities in their rotation-dispersion curves are shown by aspartic acid and its derivatives. The rotations of the so-called l -aspartic acid, its ester and the so-called l -malic acid obtained indirectly from it tend to a positive maximum, whereas the l -chlorosuccinic acid intermediate between the aspartic and malic acids tends to a negative maximum. Therefore, l -aspartic and l -malic acids should be called d -acids. The rotation of malic acid is difficult to judge, for it depends so much on concentration. The authors have chosen 25% solutions as the maximum concentration for which the curve is normal, but it is obvious that if the direction of the rotation-dispersion curve is to be a test of the configuration, the conditions of solvent, concentration, and temperature must be so chosen that the curve is as characteristic as possible for the compound under examination.

The following table gives the specific rotations at 14° for the

Substance.	C.	D.	Hg.	F.
New designation	656.3	589.3	546.3	486.1 $\mu\mu$
d -Glutamic acid	+8.05°	+10.52°	+12.96°	+17.53°
Ethyl d -pyroglutamate	-3.40	-2.68	-1.59	+1.99
l - α -Chloroglutaric acid	-18.26	-22.67	-26.81	-34.67
d - α -Hydroxyglutaric acid	-2.00	-1.34	-0.67	+0.67
Silver d -butyrolactone- γ -carb- oxylate	+5.67	+8.59	+9.14	+13.16
* d -Butyrolactone- γ -carboxylic acid	+1.11	+2.14	+2.83	+3.66
†	-0.33	+2.67	+3.33	+4.17
‡ Zinc d - α -hydroxyglutarate.....	+4.24	+6.65	+8.24	—
§ d -Aspartic acid.....	-3.54	-2.48	-2.13	—
Ethyl d -aspartate	+0.98	+1.73	+2.25	+3.38
l -Chlorosuccinic acid	-15.04	-18.92	-22.96	-30.90

* From zinc- α -hydroxyglutarate.

† From the silver salt.

‡ At 16° .

§ In dil. NaOH (3 mol.).

principal lines; for others, and for the curves, the original should be consulted.

J. C. W.

Bile Acids. V. The Reduction of Dehydrocholic and Dehydrodeoxycholic Acids. HEINRICH WIELAND and ERICH BOERSCH (*Zeitsch. physiol. Chem.*, 1919, 106, 190—201).—*Dehydroisodeoxycholic acid* (β -diketocholanic acid), $C_{24}H_{36}O_4$, was prepared as its ethyl ester by reducing an alcoholic solution of dehydrocholic acid with granulated zinc and hydrochloric acid in presence of mercuric chloride; it crystallises in colourless needles, m. p. 177°; the *ethyl* ester forms lustrous needles, m. p. 152·5°.

Cholanic acid, $C_{24}H_{40}O_2$, is obtained from dehydrocholic acid by boiling with zinc amalgam and concentrated hydrochloric acid for twelve hours, and then passing hydrogen chloride into the boiling solution for ten hours. The *ethyl* ester crystallises in shining fragments, m. p. 93—94°, $[\alpha]_D^{20} + 20\cdot97^\circ$. The acid forms voluminous clusters of needles, m. p. 163—164°, $[\alpha]_D^{20} + 21\cdot74^\circ$ in chloroform solution.

α -Ketocholanic acid, $C_{24}H_{38}O_3$, is obtained as the ethyl ester, by reducing an alcoholic solution of dehydrodeoxycholic acid with zinc amalgam and concentrated hydrochloric acid. The *ethyl* ester forms colourless needles, m. p. 95°; the acid crystallises in broad, colourless leaves, m. p. 183°.

Hydroxyketocholanic acid, $C_{24}H_{38}O_4$, also obtainable by reduction of dehydrodeoxycholic acid, forms soft, lustrous needles, m. p. 161°; the *ethyl* ester forms lustrous prisms, m. p. 133°.

S. S. Z.

The Oxidation of Organic Compounds with Alkaline Potassium Permanganate. I. The Oxidation of Acetaldehyde. II. The Oxidation of Ethylene Glycol, Glycolaldehyde, Glyoxal, Glycollic Acid, and Glyoxylic Acid.

WILLIAM LLOYD EVANS and HOMER ADKINS (*J. Amer. Chem. Soc.*, 1919, 41, 1385—1414. Compare this vol., i, 514).—I. A solution of potassium permanganate, containing 15 grams per litre and various proportions of potassium hydroxide, was reduced by a 2-molar solution of acetaldehyde at 25°, 50°, and 75°, the quantity of aldehyde being recorded, and also the weights of the various oxidation products. The results are tabulated and reproduced by curves. Within certain limits, the quantity of acetic acid produced is a function of the concentration of potassium hydroxide. When plotted on logarithmic paper, the concentrations fall on a straight line, from which the equation $\log Y = \log B - a \log X$ may be deduced, where Y = the number of grams of acetic acid produced by the oxidation of 0·1 gram-mol. of acetaldehyde at a concentration of X grams of potassium hydroxide per litre and a = the tangent of the angle which the line makes with the X axis. The limits are as follows: at 25°, 1·95 to 90 grams; at 50°, 1·3 to 32·5 grams; at 75°, 0·85 to 18·5 grams. Below the smaller values, the

oxidation to acetic acid is quantitative; above the higher values, the concentration of alkali has no influence on the yield of acetic acid. Within these limits, the yield of acetic acid decreases with increasing alkalinity and rise of temperature. The other oxidation products are oxalic acid and carbon dioxide. These increase with rise of temperature and alkalinity, but again there are limits above which the concentration of alkali is immaterial. The most instructive reproduction of the yields of these products is given in curves connecting the alkali concentrations with the weights of oxalic acid or carbon dioxide which would be produced if 0.1 molar quantities of acetaldehyde or an intermediate compound were oxidised to oxalic acid and carbon dioxide in the ratio in which they are produced in the particular experiment. For example, if in a given experiment 1 gram of oxalic acid and 1 gram of carbon dioxide were produced, the acetaldehyde equivalent would be 0.49 and 0.50 gram respectively. Then, if a total of 0.99 gram of acetaldehyde produces 1 gram of oxalic acid, 4.4 grams (0.1 mol.) would yield 4.44 grams. The ratio of oxalic acid to carbon dioxide rises with increase of temperature and alkalinity, but the curves connecting alkali concentrations with the above quantities are straight lines if plotted on logarithmic paper. That is, the weight of substance converted into oxalic acid or carbon dioxide compared with the total amount converted into oxalic acid plus carbon dioxide is a simple function of the alkali concentration. In other words, the alkali acts in the same general way on the precursor of these products as it does on the acetaldehyde from which the acetic acid is formed.

II. The oxidation of ethylene glycol, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid was studied at 50° in the same manner. Ethylene glycol yields carbon dioxide and oxalic acid; with less than 0.5 gram of potassium hydroxide per litre, the sole product appears to be carbon dioxide, then up to 3 grams per litre the yield of carbon dioxide falls and that of oxalic acid rises uniformly, after which the concentration of alkali has no influence on the ratio between the two products. Glycollaldehyde also produces carbon dioxide in falling amounts and oxalic acid in increasing quantities, but the yields are logarithmic functions of the alkali concentration. Glyoxal behaves more like ethylene glycol; the yields are linear functions of the alkali concentrations up to 45.5 grams potassium hydroxide per litre, when further alkali is without effect on the yields, that of oxalic acid being 76.7%. Glycollic acid yields the same proportions of oxalic acid and carbon dioxide regardless of whether the initial concentration of potassium hydroxide is 0.68 or 48 grams per litre. Glyoxylic acid corresponds with glycollaldehyde; the yields are logarithmic functions of the alkali concentrations.

The curves connecting the yields of oxalic acid and carbon dioxide at 50° with alkali concentrations are absolutely identical in the cases of acetaldehyde and glycollaldehyde. It is therefore highly probable that glycollaldehyde is an intermediate product in the oxidation of acetaldehyde by alkaline permanganate, and the

the proportion of at least two molecules of the former to one molecule of the latter, are mixed as intimately as possible, and the mixture is melted or moistened with strong alcohol and dried at 100—115°. In either case, the proportion of two molecules of dextrose may be exceeded, whereby the mass becomes more easily melted or pulverised. The double compound, $(C_6H_{12}O_6)_2.NaI$, exists in the anhydrous and hydrated states ($+H_2O$). In the former condition it is not hygroscopic, whilst in the latter state it is as hygroscopic as sodium iodide. The yield of the anhydrous substance is quantitative, whilst that obtained in accordance with D.R.-P. 196605 (A., 1908, i, 765) is considerably smaller.

H. W.

Solubility of Lactose. Action of Acids and Alkalis on Lactose. E. SAILLARD (*Chim. et Ind.*, 1919, 2, 1035—1036).—The solubility of lactose at various temperatures was found to be as follows, the solubility of sucrose under the same conditions below given for comparison:

Temperature.	Kilo. of sugar per 1 kilo. of water.	
	Anhydrous Lactose.	Sucrose.
21.5°	0.20	2.06
28.0	0.24	2.16
38.0	0.307	2.34
48.0	0.421	2.55
57.0	0.56	2.78
65.0	0.77	3.03

Lactose is hydrolysed completely in ninety minutes when heated at 90° with 10% hydrochloric acid, but is not appreciably attacked by 10% acetic acid. When lactose is heated at 90° with 1% sodium hydroxide solution, about 64% of the alkali is neutralised and 85% of the sugar destroyed within two hours.

W. P. S.

Predominating Influence of the Degree of Dispersion of Starch Solutions on the so-called Starch Coagulation. HERMANN SALLINGER (*Kolloid Zeitsch.*, 1919, 25, 79—81).—The coagulation of solutions of soluble starch by means of ptyalin (from human saliva) has been investigated. It is shown that the coagulation takes place sooner the larger the quantity of ptyalin added, and that the amount of coagulated starch decreases, whilst the quantity of maltose formed increases with the amount of ptyalin added. A similar starch solution heated to 110° under a pressure of 1.5 atms. before treatment was coagulated much more slowly, gave about a quarter as much coagulum, but rather more maltose, than the unheated starch. The experiments show the influence of the dispersity on the coagulation, and they also confirm the view of Lintner that it is unnecessary to assume the presence of an enzyme amylocoagulase in malt extract which is capable of affecting the coagulation of starch. The coagulation is brought about by the conversion of the protecting colloid, the starch sol, into sugar, which thereby causes the starch gel to coagulate.

J. F. S.

Synthesis of Polypeptides of which Cystine forms a Constituent. E. ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 296—309).—The following polypeptides have been synthesised:

Dichloroacetyl-L-cystine crystallises from ethyl acetate in clusters of fan-shaped prisms, m. p. 137—139°, or from water in silky spheres of long needles with one molecule of water, m. p. 96—98°. It shows weak mutarotation.

Diglycyl-L-cystine, a white, amorphous powder, decomposes at 200°, and has $[\alpha]_D^{25} -111.4^\circ$ to -116.54° in aqueous solution.

Di- α -bromo-D-isohexoyldiglycyl-L-cystine is a yellowish-white powder, and in alcoholic solution has $[\alpha]_D^{19} -8.37^\circ$ to -18.2° .

Di-L-leucyldiglycyl-L-cystine turns brown at 220°, and in aqueous solution has $[\alpha]_D^{18} -78.6^\circ$ to -80.99° .

Dichloroacetyldi-L-leucyldiglycyl-L-cystine is a light yellow powder, and in alcoholic solution has $[\alpha]_D -32.8^\circ$ to -42.85° .

Diglycyldi-L-leucyldiglycyl-L-cystine, a light yellow powder, has in aqueous solution $[\alpha]_D^{20} -81.78^\circ$.

Dibromo-D-isohexoyldiglycyldi-L-leucyldiglycyl-L-cystine forms a yellow powder.

The action of alcoholic-aqueous ammonia and of alcoholic ammonia on dichloroacetyl-L-cystine is described. S. S. Z.

Bile Acids. IV. The Synthesis of Glycodeoxycholic and Taurodeoxycholic Acids. HEINRICH WIELAND [with FR. HEDWIG STENDER] (*Zeitsch. physiol. Chem.*, 1919, **106**, 181—190. Compare A., 1916, i, 710).—*Deoxycholic acid hydrazide*, $C_{24}H_{42}O_3N_2$, prepared from the acid deoxycholic ester and hydrazine hydrate, forms colourless needles, m. p. 208°. The hydrazide was then converted into the amorphous *azide* by treating it with hydrochloric acid and sodium nitrite. From the azide, *glycodeoxycholic acid* was synthesised by a modification of the method which Bondi and Müller used in the preparation of glycocholic acid; it forms colourless needles, m. p. 187—188° (decomp.), and contains one molecule of water, which is lost on heating at 150° in a vacuum.

Taurodeoxycholic acid, $C_{33}H_{56}O_5 \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot SO_3H$, was prepared from deoxycholic acid azide in the form of colourless, hygroscopic, prismatic needles grouped in rosettes, m. p. 175—200°, not sharp.

Attempts to prepare glycocholic and taurocholic acids by combining the conjugated deoxycholic acids with stearic acid failed. The nature and origin of the glycocholic and taurocholic acids prepared from the bile are discussed. S. S. Z.

Crystallography of some Platinithiocyanates of Organic Bases. E. QUERCIGH (*Riv. Min. Crist. Ital.*, 1915, **44**, 17—25).—The guanidine salt is trigonal, the piperidine salt hexagonal-pyramidal, and the diacetoneamine salt monoclinic. Complete crystallographic data are given. CHEMICAL ABSTRACTS.

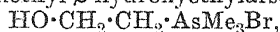
Oxidation Potential of Ferri-Ferrocyanide Solution. I. M. KOLTHOFF (*Chem. Weekblad*, 1919, **16**, 1406—1415).—The influence of the hydrogen ions on the oxidation potential of solutions of potassium ferri-ferrrocyanide has been investigated by the author. A considerable increase of potential was obtained by the addition of even 0.012*N*-hydrogen chloride, and, taking the average for various determinations with different concentrations of hydrochloric acid, it was found that $\epsilon = 0.416 - 0.0577 \log (\text{HCl})^{2.22}$. The influence of the acid is explained by the fact that the third and fourth dissociation constants of hydroferrocyanic acid are comparatively small, whilst hydroferricyanic acid is a strong acid. The concentration of the ferrocyanide ions thus becomes much lower on acidifying. The fourth dissociation constant of hydroferrocyanic acid is about 5×10^{-4} .

The author found no difference in the physical properties (except the colour) of solutions of α - and β -potassium ferrocyanide.

References to the results of other investigators are given.

W. J. W.

Ethanoltrialkylarsonium Hydroxides. M. GUGGENHEIM and E. HUG (U.S. Pat. 1308413).—Trimethyl- β -bromoethylarsonium bromide, prisms, m. p. 239° , is prepared by heating 5 parts of trimethylarsine and 7.5 parts of ethylene dibromide for three hours at about 100° . Three parts of this product may be hydrolysed by heating with 10 parts of water at 180° for four hours. Ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] bromide,



thus formed, is converted into the free base by the action of silver oxide. β -Bromotetraethylarsonium bromide, prismatic crystals, m. p. 225° , may be obtained similarly from triethylarsine. The product may be hydrolysed to form β -hydroxytetraethylarsonium bromide, and the latter can be converted into the free base by the action of silver oxide. Trimethyl- β -hydroxyethylarsonium hydroxide is a syrup which partly crystallises and has an odour like that of trimethylarsine. It is readily soluble in water or alcohol, and forms a crystalline chloride, m. p. 220° , which is soluble in alcohol.

CHEMICAL ABSTRACTS.

Ethanoltrialkylarsonium Compounds. M. GUGGENHEIM and E. HUG (U.S. Pat. 1308414).—Eighteen parts of trimethylarsine and 20 parts of ethylene chlorohydrin are heated together at 120 — 125° for four hours. The product, which is partly solidified, is dissolved in alcohol, and, after concentration of the solution, ether is added to precipitate ethanoltrimethylarsonium [trimethyl- β -hydroxyethylarsonium] chloride, $\text{OH} \cdot \text{C}_2\text{H}_4 \cdot \text{AsMe}_3 \cdot \text{Cl}$, which may be converted into the hydroxide by the action of silver oxide. Ethylene bromohydrin may be used instead of the chlorohydrin in effecting the reaction. Triethylarsine, when used as starting material, yields similar products, containing ethyl instead of

methyl. The ethanoltrialkylarsonium hydroxides and their salts are stated to possess valuable therapeutic properties.

CHEMICAL ABSTRACTS.

Relations between the Constitution and the Physical Properties of the Hydrocarbons of the Benzene Series.

K. von AUWERS (*Annalen*, 1919, **419**, 92—120. Compare A., 1916, i, 130).—Examination of the physical constants of twenty-four hydrocarbons has shown that the compounds with ortho-side-chains occupy a peculiar position; whilst the density and refractive index are higher than those of their isomerides, the exaltations of refractive and dispersive power are lower. In general, the boiling points of ortho-derivatives are higher than those of the isomeric hydrocarbons, although the differences are frequently small. The differences between the constants of ortho- and vicinal derivatives and those of their isomerides are much greater than the small discrepancies observed between different specimens of the same substance as far as carefully purified material and accurate observation are concerned. The influences of constitution on the refractive and dispersive powers of position isomeric aromatic hydrocarbons can only be detected with certainty in the cases of substances with neighbouring side-chains; the differences caused in the meta- and para-series lie within the limits of experimental error.

The methods chiefly used in the preparation of the hydrocarbons are the Fittig synthesis, the elimination of amino-groups from the corresponding amines by Friedländer's method, and the reduction of suitable ketones with amalgamated zinc and hydrochloric acid according to Clemmensen. The following constants are recorded.

Benzene has b. p. 80° , D_4^{15} 0.8867, D_4^{20} 0.880, $n_D^{15.3}$ 1.50119, $n_D^{12.3}$ 1.50565, $n_D^{12.3}$ 1.51817, $n_D^{12.3}$ 1.52867, n_D^{20} 1.5022. Toluene has b. p. $109-110^{\circ}$, $D_4^{16.35}$ 0.8684, D_4^{20} 0.866, $n_D^{16.35}$ 1.49365, $n_D^{16.35}$ 1.49782, $n_D^{16.35}$ 1.50967, $n_D^{16.35}$ 1.51970, n_D^{20} 1.4962. Ethylbenzene has b. p. $135-136^{\circ}$, $D_4^{14.5}$ 0.8708, D_4^{20} 0.866, $n_D^{14.5}$ 1.49423, $n_D^{14.5}$ 1.49828, $n_D^{14.5}$ 1.50953, $n_D^{14.5}$ 1.51904, n_D^{20} 1.4960. Propylbenzene has b. p. $158-159^{\circ}$, $D_4^{12.25}$ 0.8681, D_4^{20} 0.862, $n_D^{12.25}$ 1.49176, n_D^{20} 1.49549, $n_D^{12.25}$ 1.50630, $n_D^{12.25}$ 1.51533, n_D^{20} 1.4920. *iso*Propylbenzene has b. p. $152.8-153.4^{\circ}$, $D_4^{16.8}$ 0.8662, D_4^{20} 0.864, $n_D^{16.8}$ 1.49063, $n_D^{16.8}$ 1.49441, $n_D^{16.8}$ 1.50539, $n_D^{16.8}$ 1.51466, n_D^{20} 1.4930.

For *o*-xylene the following data are given: I. Commercial specimen rectified over sodium, b. p. $142-142.5^{\circ}$, $D_4^{17.9}$ 0.8798, D_4^{20} 0.878, $n_D^{17.9}$ 1.50090, $n_D^{17.9}$ 1.50491, $n_D^{17.9}$ 1.51668, $n_D^{17.9}$ 1.52659, n_D^{20} 1.5040. II. Specimen from *o*-iodotoluene, methyl iodide, and sodium in warm ethereal solution: b. p. 142° , $D_4^{16.1}$ 0.8825, D_4^{20} 0.879, $n_D^{16.1}$ 1.50248, $n_D^{16.1}$ 1.50664, $n_D^{16.1}$ 1.51846, $n_D^{16.1}$ 1.52838, n_D^{20} 1.5049. III. Specimen from pure *o*-3-xylydine through the diazo-compound: b. p. $142-143^{\circ}$, $D_4^{15.5}$ 0.8837, D_4^{20} 0.880, $n_D^{15.5}$ 1.50368, $n_D^{15.5}$ 1.50777, $n_D^{15.5}$ 1.51960, $n_D^{15.5}$ 1.52958, n_D^{20} 1.5057. *m*-Xylene, prepared from *m*-xylylic acid, has b. p. $135-136^{\circ}$, $D_4^{17.2}$ 0.8666, $D_4^{17.1}$ 0.8667, D_4^{20} 0.864, $n_D^{17.1}$ 1.49429, $n_D^{17.1}$ 1.49880, $n_D^{17.1}$ 1.51007, $n_D^{17.1}$ 1.51997, n_D^{20} 1.4970, whilst when prepared from *m*-xylydine it has b. p. 137.5° , $D_4^{14.85}$ 0.8686,

D_4^{20} 0.865, $n_a^{14.85}$ 1.49548, $n_D^{14.85}$ 1.49962, $n_\beta^{14.85}$ 1.51128, $n_\gamma^{14.85}$ 1.52112, n_D^{20} 1.4973. For *p*-xylene the following constants are recorded: I. Museum specimen, b. p. 135—136°, $D_4^{17.2}$ 0.8627, $D_4^{17.5}$ 0.8625, D_4^{20} 0.861, $n_a^{17.5}$ 1.49273, $n_D^{17.5}$ 1.49682, $n_\beta^{17.5}$ 1.50849, $n_\gamma^{17.5}$ 1.51841, n_D^{20} 1.4957. II. Kahlbaum's product distilled over sodium, b. p. 136—137°, $D_4^{16.1}$ 0.8659, $D_4^{16.2}$ 0.8658, D_4^{20} 0.863, $n_a^{16.2}$ 1.49357, $n_D^{16.2}$ 1.49760, $n_\beta^{16.2}$ 1.50925, $n_\gamma^{16.2}$ 1.51907, n_D^{20} 1.4959. III. Specimen from *p*-dibromobenzene, b. p. 135—136°, $D_4^{16.2}$ 0.8624, D_4^{20} 0.859, $n_a^{16.2}$ 1.49335, $n_D^{16.2}$ 1.49734, $n_\beta^{16.2}$ 1.50912, $n_\gamma^{16.2}$ 1.51902, n_D^{20} 1.4956.

o-Methylethylbenzene has b. p. 164.8—165°, $D_4^{15.7}$ 0.8841, D_4^{20} 0.881, $n_a^{15.7}$ 1.50213, $n_D^{15.7}$ 1.50611, $n_\beta^{15.7}$ 1.51745, $n_\gamma^{15.7}$ 1.52693, n_D^{20} 1.5042. *m*-Methylethylbenzene has b. p. 161.5—162.5°, $D_4^{17.9}$ 0.8690, D_4^{20} 0.867, $n_a^{17.9}$ 1.49456, $n_D^{17.9}$ 1.49849, $n_\beta^{17.9}$ 1.50973, $n_\gamma^{17.9}$ 1.51920, n_D^{20} 1.4975. *p*-Methylethylbenzene (from *p*-bromotoluene) has b. p. 161—162°, $D_4^{22.3}$ 0.8601, $D_4^{22.8}$ 0.8597, D_4^{30} 0.862, $n_a^{22.8}$ 1.48921, $n_D^{22.8}$ 1.49303, $n_\beta^{22.8}$ 1.50417, $n_\gamma^{22.8}$ 1.51353, n_D^{30} 1.4943, whilst when prepared from *p*-tolyl methyl ketone it has b. p. 161—162°, $D_4^{13.1}$ 0.8687, ($D_4^{13.4}$ 0.8685), D_4^{20} 0.863, $n_a^{13.4}$ 1.49588, $n_D^{13.4}$ 1.50004, $n_\beta^{13.4}$ 1.51136, $n_\gamma^{13.4}$ 1.52116, n_D^{20} 1.4971.

o-Methylpropylbenzene has b. p. 184°, $D_4^{15.75}$ 0.8770, D_4^{20} 0.874, $n_a^{15.75}$ 1.49765, $n_D^{15.75}$ 1.50139, $n_\beta^{15.75}$ 1.51218, $n_\gamma^{15.75}$ 1.52125, n_D^{20} 1.4995. *m*-Methylpropylbenzene has b. p. 181.5—182.5°, D_4^{17} 0.8648, D_4^{20} 0.862, n_a^{17} 1.49262, n_D^{17} 1.49640, n_β^{17} 1.50738, n_γ^{17} 1.51646, n_D^{20} 1.4951. *p*-Methylpropylbenzene has b. p. 182—183°, $D_4^{15.4}$ 0.8642, D_4^{20} 0.861, $n_a^{15.4}$ 1.49371, $n_D^{15.4}$ 1.49749, $n_\beta^{15.4}$ 1.50863, $n_\gamma^{15.4}$ 1.51804, n_D^{20} 1.4954.

o-Methylisopropylbenzene (*o*-cymene) has b. p. 175—176°, $D_4^{16.15}$ 0.8789, D_4^{20} 0.876, $n_a^{16.15}$ 1.49826, $n_D^{16.15}$ 1.50206, $n_\beta^{16.15}$ 1.51290, $n_\gamma^{16.15}$ 1.52185, n_D^{20} 1.5003. *m*-Methylisopropylbenzene has b. p. 175°, $D_4^{17.05}$ 0.8628, D_4^{20} 0.860, $n_a^{17.05}$ 1.49016, $n_D^{17.05}$ 1.49385, $n_\beta^{17.05}$ 1.50452, $n_\gamma^{17.05}$ 1.51336, n_D^{20} 1.4925. *p*-Methylisopropylbenzene, from toluene, isopropyl bromide, and aluminium chloride, has b. p. 175—176°, $D_4^{15.0}$ 0.8631, D_4^{20} 0.859, n_a^{15} 1.49105, n_D^{15} 1.49474, n_β^{15} 1.50537, n_γ^{15} 1.51449, n_D^{20} 1.4925; the physical constants are also recorded for specimens obtained commercially, from camphor and phosphoric oxide, from α -terpineol by Wallach's method, and from 1-methyl-4- $\beta\beta$ -dichloroisopropylbenzene by reduction with sodium and alcohol.

p-Diethylbenzene has b. p. 183°, $D_4^{16.3}$ 0.8678 ($D_4^{16.2}$ 0.8679), D_4^{20} 0.865, $n_a^{16.2}$ 1.49499, $n_D^{16.2}$ 1.49897, $n_\beta^{16.2}$ 1.50993, $n_\gamma^{16.2}$ 1.51924, n_D^{20} 1.4973. Hemimellitene has b. p. 175—176°/744 mm., $D_4^{19.55}$ 0.8949, D_4^{20} 0.895, $n_a^{19.55}$ 1.50930, $n_D^{19.55}$ 1.51335, $n_\beta^{19.55}$ 1.52503, $n_\gamma^{19.55}$ 1.53483, n_D^{20} 1.5132. ψ -Cumene has b. p. 168.7—169.2°, $D_4^{15.3}$ 0.8794, D_4^{20} 0.876, $n_a^{15.3}$ 1.50259, $n_D^{15.3}$ 1.50672, $n_\beta^{15.3}$ 1.51841, $n_\gamma^{15.3}$ 1.52816, n_D^{20} 1.5046. Mesitylene has b. p. 165—166°, $D_4^{17.05}$ 0.8646, D_4^{20} 0.862, $n_a^{17.05}$ 1.49403, $n_D^{17.05}$ 1.49804, $n_\beta^{17.05}$ 1.50936, $n_\gamma^{17.05}$ 1.51891, n_D^{20} 1.4967.

1:2:3:4-Tetramethylbenzene has b. p. 203—204°, D_4^{16} 0.9044, D_4^{20} 0.901, n_a^{16} 1.51621, n_D^{16} 1.52031, n_β^{16} 1.53192, n_γ^{16} 1.54189, n_D^{20} 1.5185. 1:2:5-Trimethyl-4-ethylbenzene has b. p. 211°, $D_4^{15.85}$ 0.8866, ($D_4^{15.75}$ 0.8867), D_4^{20} 0.883, $n_a^{15.75}$ 1.50654, $n_D^{15.75}$ 1.51047, $n_\beta^{15.75}$ 1.52163, $n_\gamma^{15.75}$ 1.53112, n_D^{20} 1.5086. 1:3:5-Trimethyl-2-ethylbenzene has b. p. 210.2°/753 mm., $D_4^{16.35}$ 0.8885, D_4^{20} 0.886, $n_a^{16.35}$ 1.50875, $n_D^{16.35}$ 1.51274, $n_\beta^{16.35}$ 1.52416, $n_\gamma^{16.35}$ 1.53376, n_D^{20} 1.5111. H. W.

Pyro-condensations in the Aromatic Series. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1916, **37**, 681—722).—The first of three papers on this subject, the second having already been reviewed in A., 1917, i, 641, and the third in A., 1918, i, 66. The object of the initial investigation was to study the products formed by the decomposition of the vapours of non-halogenated aromatic compounds at the lowest possible temperatures, the method being similar to that described in a series of papers by Löb (1901—1905).

Benzene begins to decompose into diphenyl at 650° (compare Smith and Lewcock, T., 1912, **101**, 1453).

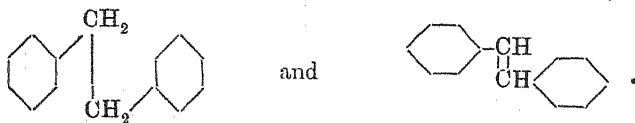
When kept for a few hours at a dull red heat, toluene vapour gives almost exclusively dibenzyl, the product which is formed when toluene is oxidised with potassium persulphate in the cold (Moritz and Wolfenstein, A., 1899, i, 424). At a bright red heat, however, hydrogen is also lost from the nucleus. The hydrocarbons which may be frozen out from the mixture at -80° include dibenzyl, stilbene, and anthracene (see below), whilst a study of the oxidation products of the remaining oil reveals the probable presence of di-*p*-tolyl and *p*-methyl-diphenylmethane.

At a bright red heat, *p*-xylene readily yields *p*-dixyl, $C_6H_4Me \cdot CH_2 \cdot CH_2 \cdot C_6H_4Me$, m. p. 81—82° (*ibid.*), but at a higher temperature (yellow heat) more oil is produced. The chief by-product is *pp'*-dimethylstilbene.

Mesitylene decomposes very smoothly, giving dimesityl.

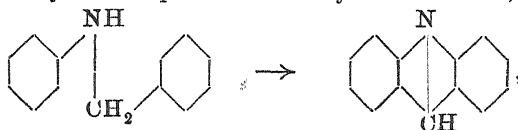
Ethylbenzene gives chiefly stilbene and an oily by-product, which only yields benzoic acid on oxidation, and therefore contains no hydrocarbons with condensed nuclei. The production of stilbene may be due to the elimination of methane and the union of the $:CHPh$ residues, or to condensation to β -diphenylbutane and loss of ethylene.

Dibenzyl gives stilbene and a very little toluene, with considerable quantities of anthracene, but no trace of phenanthrene. Stilbene, however, gives no anthracene or phenanthrene. This remarkable difference between dibenzyl and stilbene is explained by assuming that the positive methylene groups in the former bring the negative benzene nuclei close to the connecting chain, whereas the negative ethylene linking in stilbene keeps the nuclei at a distance, thus:

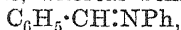


Several facts support this idea. In the first place, dihydroanthracene, which should be the primary product from dibenzyl, passes rapidly into anthracene at a red heat, and *p*-xylene or *p*-dixyl gives 2:6-dimethylantracene at a bright red heat,

whereas mesitylene or dimesityl forms no anthracene derivative. Similarly, benzylaniline passes so readily into acridine,



that this pyrogenic method may be employed with advantage in the preparation of acridine, whereas benzyldeneaniline,



only yields aniline, benzonitrile, benzene, diphenyl, and such products.

Benzanilide gives a good yield of phenanthridone, m. p. 290° , which is reduced to phenanthridine by distillation over zinc dust.

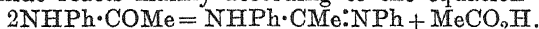
When diphenylmethane vapour is exposed to the glowing platinum spiral for seven hours, the products are benzene, toluene, a trace of diphenyl, and small quantities of anthracene, but chiefly fluorene, the process ranking as a convenient synthesis of this hydrocarbon. It is stated that Carnelley's " γ -methylenediphenyl" is only fluorene, and his " δ -methylenediphenyl" is most probably anthracene (T., 1880, **37**, 708).

Benzophenone is not easily changed, but the initial products are benzene and benzaldehyde.

Diphenyl ether readily yields diphenylene oxide, m. p. 81° .

Diphenylamine gives carbazole and some hydrogen cyanide, but di- α -naphthylamine loses ammonia and forms naphthalene instead of a substituted carbazole.

Acetanilide reacts mainly according to the equation



The bases are extracted from the ethereal solution of the product and then submitted to distillation in steam, when small quantities of aniline and *o*-aminoacetophenone (recognised by its jasmine-like odour) pass over, leaving a little *p*-aminoacetophenone and the diphenylethylenamidine behind.

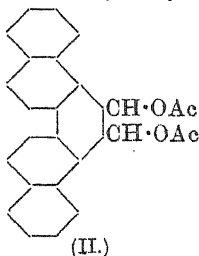
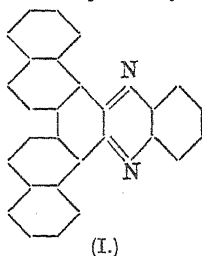
Naphthalene decomposes into $\beta\beta$ -dinaphthyl at a dull red heat, but as the temperature is raised more and more $\alpha\alpha$ -dinaphthyl is formed. The so-called $\alpha\beta$ -dinaphthyl (Smith, T., 1877, **32**, 559; Wegscheider, A., 1891, 216) is probably impure $\alpha\alpha$ -dinaphthyl.

Diphenyl gives 4:4'-diphenyldiphenyl, $\text{C}_6\text{H}_5\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_5$, m. p. 310° . *o-o'*-Ditolyl, from *o*-iodotoluene by heating with copper at 250° , reacts rapidly at the glowing spiral to form phenanthrene, which apparently gives diphenanthryl when the heating is continued. Anthracene gives 5:5'-dianthryl, but anthraquinone residues link up in the 2:2'-positions.

Weger reported the production of naphthalene by the passage of cyclopentadiene vapours through a red-hot tube (*Zeitsch. angew. Chem.*, 1909, **22**, 344), but this must have been due to the total disruption of the molecule and rebuilding from the ethylene and acetylene produced. Under the present conditions, no naphthalene

could be found, the products being partly evil-smelling oils and partly soluble or insoluble, but amorphous, solids.

The so-called "*Crackene*" [with PAUL R. VON LENDENFELD].—Klaudy and Fink (A., 1900, i, 284) isolated "*crackene*" from the so-called red pitch formed in the "*cracking*" of oils, and suggested that it might be identical with "*benzerythrene*," since proved to be the above 4:4'-diphenyldiphenyl, but certainly not with picene. The present authors were struck with the fact that various fractions of the hydrocarbon varied slightly in colour. By treatment with a small quantity of bromine in warm chloroform, followed by repeated crystallisations from boiling xylene, they have succeeded in removing a coloured impurity and establishing the substance as picene. Picene may be characterised by conversion into picenequinone, and formation from this of *picenequinoraline* (I), microscopic, yellow needles, by condensation with *o*-phenylenediamine. Picenequinone also forms a yellowish-brown *diacetyl* derivative (II), which may be hydrolysed to a dark dihydroxy-derivative.



The acetylation is therefore accompanied by reduction. Picene and benzerythrene are said to dissolve in concentrated sulphuric acid with green colour. The pure hydrocarbons really give colourless solutions, picene exhibiting pale blue fluorescence.

J. C. W.

The cycloPropane Series. VII. Nitrocyclopropanes. E. P. KOHLER and H. F. ENGELBRECHT (*J. Amer. Chem. Soc.*, 1919, 41, 1379—1384. Compare this vol., i, 533).—Phenyl styryl ketone condenses with nitromethane to form phenyl γ -nitro- β -phenylpropyl ketone, which yields two α -bromo-derivatives when treated with bromine in chloroform. The principal product has m. p. 100°, and is transformed into the isomeride, m. p. 106° (not 86°, as given in A., 1916, i, 404), by crystallising from an alcoholic solution of hydrogen bromide. The bromides,

$\text{NO}_2 \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{CHBr} \cdot \text{CH}_2 \cdot \text{COPh}$,

readily change into 3-nitro-1-benzoyl-2-phenylcyclopropane, $\text{NO}_2 \cdot \text{CH} \begin{smallmatrix} \text{CHBr} \\ \text{CHPh} \end{smallmatrix}$, when treated with an alcoholic solution of potassium acetate. The compound crystallises in clusters of stout prisms, m. p. 98°, and is changed by the action of hydrogen bromide dissolved in acetic acid into phenyl γ -bromo- β -nitro- γ -phenylpropyl ketone, $\text{CHPhBr} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH}_2 \cdot \text{COPh}$, which forms colourless plates, m. p. 115—116°, and becomes yellow in sunlight. This

ketone is very sensitive. When boiled with methyl alcohol and a little ammonium bromide, for example, it changes into 2:5-diphenylfuran, and when heated above its m. p. it gives a pale yellow substance, plates, m. p. 77°, which is probably 3-bromo-1:5-diphenylfuran. The cyclopropane derivative reacts most readily with bases, but the products are complex mixtures. With sodium methoxide solution, under special conditions, it is possible to isolate $\alpha\delta$ -diphenylbutan- $\alpha\gamma$ -dione, $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{COPh}$. J. C. W.

Decomposition of Tetranitromethylaniline [2:4:6-Trinitrophenylmethylnitroamine]. EDMUND VON HERZ (*Z. ges. Schiess. u. Sprengstoffw.*, 1919, **14**, 155—157; from *Chem. Zentr.*, 1919, iv, 163).—The author's previous conclusion that the decomposition can be caused by electrolytic processes is confirmed by further laboratory experiments. Diazo-compounds similar to dinitrobenzoquinonediazide are probably formed, and not azide

substances, such as $\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2 < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$. It is certain that the reac-

tions which result in the decomposition products affect the benzene nucleus exclusively; the occurrence of ammonia, methylamine, etc., is due solely to secondary changes, and has no influence on the characteristic transformation of the nucleus. The observed phenomena are not a specific property of tetryl, but are common to all trinitro-derivatives of benzene, such as trinitro-benzene, -toluene, -phenol, and -cresol. Decompositions of mercury fulminate in zinc capsules covered with an inner cap of copper or brass are probably also to be attributed to local electric currents. H. W.

Proteinogenous Amines. V. The Preparation of *p*-Hydroxyphenylethylamine Hydrochloride (Tyramine Hydrochloride). KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, **39**, 585—592).—Certain improvements in the method for the synthesis of *p*-hydroxyphenylacetone nitrile as given by Pschorr, Wolfes, and Buckow (*A.*, 1900, i, 170) are recorded. The reduction of this substance is effected by a method which it is claimed is more satisfactory than that employed by Barger (*T.*, 1909, **95**, 1127). The *p*-hydroxyphenylacetone nitrile is dissolved in alcohol and treated with sodium, and after reduction is completed, the solution is rendered acid with hydrochloric acid. *p*-Cresol and *p*-hydroxyphenylacetic acid may then be removed by extraction with ether, after which the solution is rendered strongly alkaline and the tyramine is extracted with amyl alcohol. The amine may be extracted from the amyl alcohol by shaking with dilute hydrochloric acid. Yield, 58% of theoretical. The *p*-cresol and *p*-hydroxyphenylacetic acid present in the ethereal extract may be separated and isolated by shaking with sodium carbonate solution. The ethereal fraction retains the *p*-cresol, whilst the alkaline aqueous solution removes the *p*-hydroxyphenylacetic acid. J. C. D.

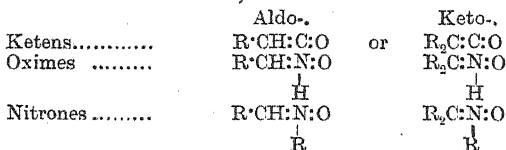
The Problem of the Physiological Polypeptide Synthesis. EMIL ABDERHALDEN and HANS SPINNER (*Zeitsch. physiol. Chem.*, 1919, **106**, 309—312).—By treating glycine with benzaldehyde in

absolute alcohol and sodium hydroxide, a condensation product identical with the benzylidene compound of *isodiphenyloxethylamine* is obtained in small needles, m. p. 132°. By treating glycine dissolved in sodium hydroxide with benzaldehyde and then oxidising with potassium permanganate, benzoic and hippuric acids are obtained. S. S. Z.

Dialkyldiarylcarbamides. H. WINKEL (U.S. Pat. 1307570).—By conducting the reaction at 80—90°, diphenyldimethylcarbamide is prepared by passing carbonyl chloride directly into a mixture of methylaniline and dimethylaniline (which may also contain small quantities of aniline) without the use of a solvent. Aniline, methylaniline, and dimethylaniline may be mixed, in the proportions of 10, 40, and 50 parts respectively, and this mixture treated with carbonyl chloride until conversion of the methylaniline into diphenyldimethylcarbamide is completed as indicated by cessation of absorption of carbonyl chloride. The reaction mixture is then treated with dilute hydrochloric acid for the removal of dimethylaniline, and the product remaining is washed free from acid with water. It may then be further purified by crystallisation from any suitable solvent.

CHEMICAL ABSTRACTS.

Nitrones and Nitrenes. H. STAUDINGER and KARL MIESCHER (*Helv. Chim. Acta*, 1919, 2, 554—582).—In connexion with his well-known studies of compounds with “twin bonds,” Staudinger now describes several reactions of nitrones and a new class, the nitrenes. Nitrones are comparable in structure with the tautomeric forms of oximes and with ketens, thus:

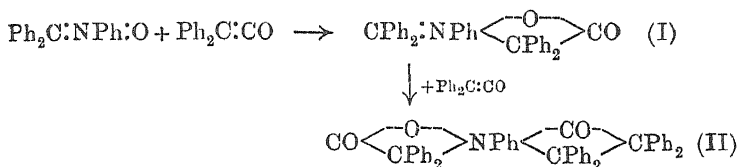


and nitrenes are comparable with allenes, thus: allenes, $R_2 C : C : CR_2$; nitrenes, $R_2 C : N : CR_2$. The simple nitrones are produced by the

alkylation of oximes, or by the action of aldehydes on *N*-substituted hydroxylamines. They are often formulated as cyclic ethers, thus, $R \cdot CH \begin{smallmatrix} \nearrow NR \\ \searrow O \end{smallmatrix}$, although the evidence in favour of the nitrone formula

(the name was proposed by Pfeiffer, A., 1916, i, 327) has become very strong in recent years (compare Forster and Holmes, T., 1908, 93, 244; Brady, T., 1914, 105, 2104; Semper and Lichtenstadt, A., 1918, i, 437). It is now found that the “keto”-nitrones, $R_2 C : NR : O$, are readily obtained by the action of aliphatic diazo-compounds on nitroso-compounds, the reaction being represented by the following scheme, although no intermediate products have been isolated: $R \cdot NO + R_2 C \begin{smallmatrix} \nearrow N \\ \searrow N \end{smallmatrix} \rightarrow RN \begin{smallmatrix} \nearrow O-N \\ \searrow CR_2 \end{smallmatrix} \rightarrow RN \begin{smallmatrix} \nearrow O \\ \searrow CR_2 \end{smallmatrix} = R_2 C : NR : O$. The presence of two double linkings in these nitrones

is revealed by the fact that they combine with diphenylketen in two stages, thus:

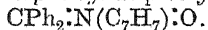


The nitrenes are formed when the products of the type I are heated, carbon dioxide being evolved. They are quite stable compounds, but capable of many reactions, of which combination with diphenylketen is particularly described.

Experiments with Diphenyldiazomethane.—Nitrosobenzene reacts with diphenyldiazomethane (A., 1916, i, 850) in ice-cold benzene to form diphenyl-*N*-phenylnitrene, $\text{CPh}_2:\text{NPh}:\text{O}$, which separates in pale yellow needles, m. p. 216—217° (decomp.) (Angeli, A., 1911, i, 544, gives m. p. 214°). The following reactions are described: (1) hydrolysis to benzophenone and *p*-aminophenol, by boiling with dilute sulphuric acid, thus: $\text{CPh}_2:\text{NPh}:\text{O} + \text{H}_2\text{O} \rightarrow \text{CPh}_2\text{O} + \text{OH}\cdot\text{NHPH} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$; (2) fission by means of hydroxylamine or phenylhydrazine, benzophenone-oxime or -phenylhydrazone being formed; (3) reduction to benzophenoneanil by heating with iron powder; (4) oxidation to benzophenone and nitrobenzene by ozonising and boiling the product with water; (5) decomposition on heating, either alone or with benzene at 250°, into benzophenone, benzophenoneanil, and nitrosobenzene. The nitrene combines with phenylcarbimide (1 mol.) in benzene to form a compound, $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$, m. p. 164—165°, which loses carbon dioxide at 210° and is reconverted into the nitrene by boiling with alcohol. The reaction with diphenylketen in cold benzene, in an atmosphere of carbon dioxide, results in the formation of the above pale yellow compound (I), m. p. 181° (carbon dioxide evolved), the second compound (II), a white, crystalline powder, m. p. 166—168°, being formed if the reaction is carried out in boiling benzene.

*Tetraphenyl-*N*-phenylnitrene*, $\text{CPh}_2:\text{NPh}:\text{CPh}_2$, is formed by heating compound (I) at 190°. It crystallises in small, yellow prisms, m. p. 137°, and may be reduced by aluminium amalgam in ether to *dibenzhydrylaniline*, $\text{NPh}(\text{CHPh}_2)_2$, which crystallises in silvery needles, m. p. 160—161°, is so feebly basic that solutions in mineral acids deposit the base on dilution, and may be synthesised by heating together benzhydrylaniline, diphenylbromomethane, and quinoline. The nitrene combines with diphenylketen to form a compound, $\text{C}_{46}\text{H}_{35}\text{ON}$, white needles, m. p. 203·5—204·5°, and with hydrogen chloride to give a compound, $\text{C}_{32}\text{H}_{26}\text{NCl}$, m. p. 163°, both products yielding the nitrene again when heated.

[With E. SCHLENKER.]—Diphenyldiazomethane reacts with *p*-nitrosotoluene to give *diphenyl-*N*-p-tolylnitrene*,

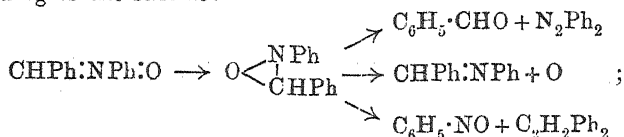


pale yellow needles, m. p. 153° (decomp.), which combines with

diphenylketen to form the compound, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{<}\begin{smallmatrix} \text{O}\cdot\text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, m. p. 161° , this decomposing at 170° into *tetraphenyl-N-p-tolyl-nitrene*, $\text{CPh}_2\text{:N}(\text{C}_7\text{H}_7)\text{:CPh}_2$, yellow crystals, m. p. 118° .

p-Nitrosodimethylaniline and diphenyldiazomethane produce *diphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\text{<}\begin{smallmatrix} \text{O} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, as a pale yellowish-green powder, m. p. $186\text{--}187^\circ$ (decomp.). This gives a yellowish-green compound, $\text{C}_{35}\text{H}_{30}\text{O}_3\text{N}_2$, with diphenylketen, which decomposes at 169° into *tetraphenyl-N-p-dimethylaminophenylnitrene*, $\text{CPh}_2\text{:N}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)\text{:CPh}_2$, orange-yellow crystals, m. p. 155° .

Experiments with other Diazo-compounds.—Diphenylenediazomethane (*ibid.*) and nitrosobenzene produce *diphenylene-N-phenylnitrene*, $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C:NPh:O}$, long, dark yellow needles, m. p. $192\text{--}193^\circ$ (decomp.), its diphenylketen compound, $\text{C}_{33}\text{H}_{23}\text{O}_2\text{N}$, pale yellow, m. p. $157\text{--}158^\circ$ (decomp.), and *diphenylenediphenyl-N-phenylnitrene*, $\begin{smallmatrix} \text{C}_6\text{H}_5 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C:NPh:CPh}_2$, obtained as an impure, green powder, m. p. $90\text{--}100^\circ$. Phenyldiazomethane and nitrosobenzene give *phenyl-N-phenylnitrene*, CHPh:NPh:O , m. p. $112\text{--}113^\circ$, which is the product obtained by the interaction of benzaldehyde and phenylhydroxylamine. This nitrene decomposes when heated according to the scheme:



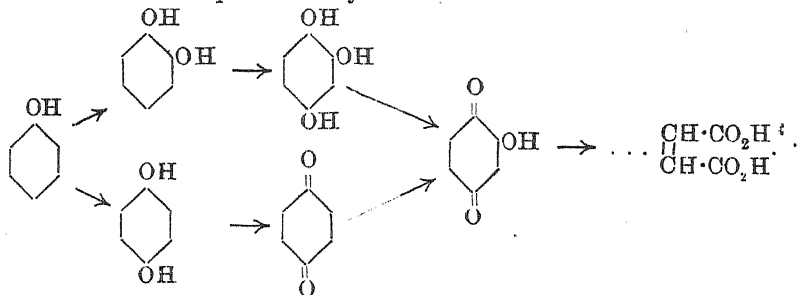
with the exception of the stilbene, all the products have been identified. The diphenylketen compound, $\text{CHPh:NPh}<\begin{smallmatrix} \text{O}\cdot\text{CO} \\ | \\ \text{CPh}_2 \end{smallmatrix}$, is a white powder, m. p. $186\text{--}190^\circ$, which decomposes on heating at 215° into *triphenyl-N-phenylnitrene*, CHPh:NPh:CPh_2 , pale yellow crystals, m. p. $105\text{--}106^\circ$, but also suffers rearrangement to a certain extent into a product, m. p. 223° , probably represented by the formula $\text{NPh}<\begin{smallmatrix} \text{CHPh}\cdot\text{CPh}_2 \\ | \\ \text{O} \text{---} \text{CO} \end{smallmatrix}$.

Ethyl diazoacetate and nitrosobenzene only react slowly and give a viscous, reddish-yellow oil, which decomposes on distillation in a vacuum into ethyl glyoxylate and azobenzene. J. C. W.

Electrochemical Oxidation of Phenols and Cresols.

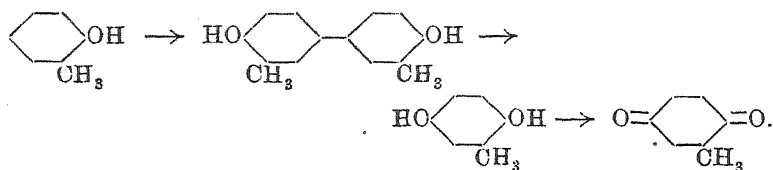
FR. FICHTER and FRANZ ACKERMANN (*Helv. Chim. Acta*, 1919, 2, 583—599).—A continuation of previously published work on the electrochemical oxidation of phenol (Fichter and Stocker, A., 1914, i, 946). It has been shown that the electrochemical oxidation of phenol produces *op*'-diphenol and *pp*'-diphenol, which are inter-

mediate products in the formation of quinol and catechol. In the present experiments, 5.5 grams of catechol dissolved in 60 c.c. of 0.5*N*-sulphuric acid were subjected to a current of 0.02 amp./cm.² between lead electrodes. When no diaphragm was used, the products consisted of carbon dioxide, carbon monoxide, a volatile liquid with an odour of butyric acid, which consists of a mixture of butyric acid and its lower homologues, particularly formic acid, and succinic acid. When a diaphragm is used, the product consists of fumaric acid. The electrochemical oxidation of phenol to fumaric acid is represented by the scheme:

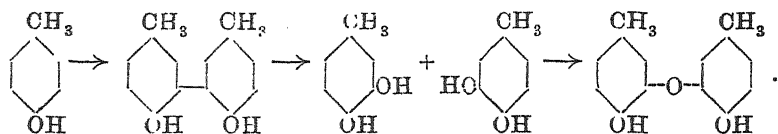


A number of experiments are described in which an attempt is made to ascertain the relative quantities of catechol and quinol produced in the electrochemical oxidation of phenol. By means of *E.M.F.* measurements, it is shown that at low concentrations quinol is a more active depolariser of a platinum electrode in 2*N*-sulphuric acid than catechol, but at concentrations above 0.05*N* the relationship is reversed. In a neutral solution, phenol has no depolarising action, and catechol has a much stronger depolarising action than quinol. In the case of a lead dioxide anode, catechol is much the strongest depolariser, so that the results allow no conclusion to be drawn as to the ratio of the two substances formed. An estimation of the amount of carbon dioxide formed in the electrolysis of phenol, catechol, and quinol, respectively, leads to the result that approximately the same quantities of quinol and catechol are formed in the electro-oxidation of phenol. An attempt to estimate directly the amount of quinol formed yielded no definite result, chiefly because of the presence of a resin in the products. The formation of the fatty acids is due to a reduction of the catechol, followed by an oxidation of the product of reduction. The reduction product of catechol is shown in a separate experiment to be *cyclohexanol*. This can be prepared by reducing a solution of 2.2 grams of catechol in 50 c.c. of 2*N*-sulphuric acid in a large platinum crucible with the anode in a porous pot. The high boiling residue of the electro-oxidation of phenol is shown to consist of diphenols, *o*-hydroxyphenyl ethers, diphenyl, tetrahydroxydiphenyl, and a dihydroxydiphenyl ether of the formula $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$. The electro-oxidation of *o*-cresol (540 grams in 2½ litres of *N*-sulphuric acid) by a current of anode density 0.0025 amp./sq. cm. without diaphragm and with vigorous

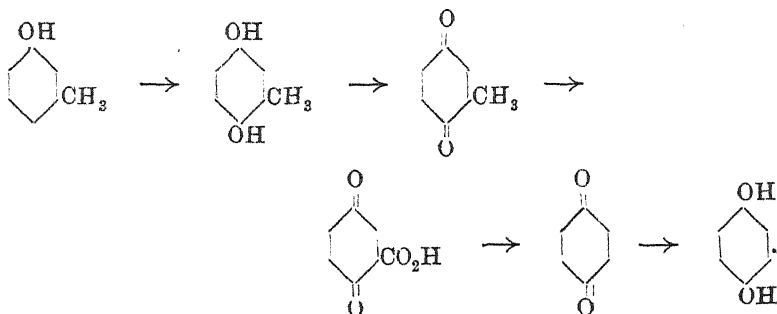
stirring gave, after 135.3 amp. hours had been passed, a dark brown oil and an aqueous solution. The oil consisted of *o*-dicresol, and the aqueous solution contained 2:5-toluquinone. The present results, together with previous work, show that the electro-oxidation of *o*-cresol may be represented by the scheme:



Similar experiments with *p*-cresol yielded from the aqueous layer toluquinone and benzoquinone, whilst the oily layer gave *p*-dicresol and 2:2'-dihydroxy-5:5'-dimethyldiphenyl ether. The formation of the latter compound is regarded as due to the loss of a molecule of water from two molecules of homocatechol. The electro-oxidation of *p*-cresol is represented by the scheme:



The formation of 2:5-toluquinone and *p*-benzoquinone in the present case is attributed to the presence of *m*-cresol in the material used. The oxidation scheme for *m*-cresol is represented as follows:



J. F. S.

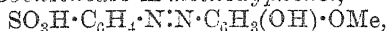
Certain Amino- and Acylamino-phenol Ethers. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1919, 41, 1450—1472).—DERIVATIVES OF PHENOL AND *o*- AND *m*-CRESOL. —Chloroaceto-*o*-anisidide, from the base by the method already described (*A.*, 1917, i, 552), has m. p. 48.5—49° (corr.). Chloroaceto-*m*-anisidide, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$, forms tufts of flat needles, m. p. 90.5—91° (corr.). Chloroaceto-*o*-phenetidide crystallises in hexagonal rhombs, m. p. 65.5—67.0° (corr.), and chloroaceto-*m*-phenetidide in glistening, flat needles, m. p.

125.5—126.5°. *Aceto-4-methoxy-m-toluidide*, large, nacreous scales, m. p. 103—103.5°, from 5-amino-*o*-cresol (A., 1917, i, 695) by acetylation and then methylation with methyl sulphate, is hydrolysed by boiling hydrochloric acid (1:1) to 4-methoxy-*m*-toluidine, m. p. 59—59.5° (Bamberger, A., 1912, i, 691), and then converted into *chloroaceto-4-methoxy-m-toluidide*, delicate needles, m. p. 90—92°. 4-Methoxy-*o*-toluidine, m. p. 13—14° (corr.), b. p. 146—147°/23 mm. (*ibid.*), is obtained by the methylation and subsequent hydrolysis of 6-acetyl-amino-*m*-cresol (A., 1917, i, 695), and converted into *chloroaceto-4-methoxy-o-toluidide*, which forms hair-like needles, m. p. 134.5—135.5°. 3-Nitro-*p*-anisidine, obtained by nitrating aceto-*p*-anisidide and hydrolysing the product, crystallises in orange-red prisms and plates, m. p. 57—57.5° (corr.), and 3-nitro-4-methoxychloroacetanilide forms golden-yellow, flat needles, m. p. 149.5—151.5°. *p*-Anisidine is sulphonated and then acetylated, yielding 3-acetyl-amino-6-methoxybenzenesulphonic acid, flat needles, which intumesce at 197—198°, then resolidify, and finally melt at 250° (decomp.). The crude sodium salt of this acid is ground with phosphorus pentachloride, and the product is converted into the *sulphonamide*, m. p. 233—235.5° (not purified), which is hydrolysed by dilute hydrochloric acid to 3-amino-6-methoxybenzenesulphonamide, radiate aggregates of creamy spindles, m. p. 184.5—186°.

DERIVATIVES OF THE ETHERS OF 4-AMINOCATECHOL.—3:4-Methylenedioxychloroacetanilide forms microscopic needles, m. p. 157.5—158.5°. 4-Aminoguaiacol (this vol., i, 265) yields 4-hydroxy-3-methoxychloroacetanilide in pale pink, nacreous plates, m. p. 113—114°. 3-Hydroxy-4-methoxychloroacetanilide also forms pale pink, nacreous plates, m. p. 140—150°. *o*-Ethoxyphenol is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzenearazoethoxyphenol, dark red plates with 2H₂O, is reduced by means of ammonium sulphide to 4-amino-6-ethoxyphenol (4-hydroxy-5-ethoxyaniline), which crystallises in minute, hexagonal plates, m. p. 186—188°. This base yields 4-hydroxy-5-ethoxyacetanilide, nacreous plates, m. p. 165.5—166.5°, and the *chloroacetanilide*, OEt·C₆H₃(OH)·NH·CO·CH₂Cl, woolly needles, m. p. 155—156°. 3:4-Dimethoxychloroacetanilide, long, silky needles, m. p. 133.5—134.5°, is obtained from 4-aminoveratrole. 4-Acetylaminoguaiacol is ethylated by means of ethyl sulphate, giving 3-methoxy-4-ethoxyacetanilide, long, narrow, nacreous plates, m. p. 148.5—150° (Freys's methoxyphenacetin?, A., 1901, i, 321). This is hydrolysed to 3-methoxy-4-ethoxyaniline, prismatic needles, m. p. 55° (corr.), b. p. 175—176°/20 mm., and then converted into the *chloroacetanilide*, long, silky needles, m. p. 133—134°. The above 4-hydroxy-5-ethoxyacetanilide is methylated and converted into 4-methoxy-5-ethoxyacetanilide, very thin, faintly purple scales, m. p. 145—146°, 4-methoxy-5-ethoxyaniline, faintly pink, rhombic crystals, m. p. 81.5—82° (corr.), and the *chloroacetanilide*, woolly needles, m. p. 135.5—136°. The same compound, on ethylation, yields 3:4-diethoxyacetanilide, m. p. 124—125.5° (Wisinger,

A., 1901, i, 205). from which 3:4-diethoxyaniline, creamy prisms, m. p. 47·5—48·5°, and 3:4-diethoxychloroacetanilide, m. p. 122·5—124·5°, may be obtained.

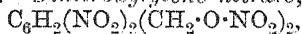
DERIVATIVES OF THE ETHERS OF RESORCINOL.—Resorcinol monomethyl ether is coupled with diazotised sulphanilic acid, and the dye, *p*-sulphobenzeneazo-*m*-methoxyphenol,



lustrous, brownish-orange platelets, with $1\text{H}_2\text{O}$, a brick-red powder, decomp. 250°, when dried, is reduced to 4-amino-5-methoxyphenol (4-hydroxy-6-methoxyaniline), pale purplish-brown needles, m. p. 175—180° (the hydrochloride is described by Henrich and Rhodius, A., 1902, i, 447). The base is converted into 4-hydroxy-6-methoxyacetanilide, pale pink aggregates of minute needles, m. p. 169—171·5°, and the chloroacetanilide, nacreous platelets, m. p. 165·5—166·5°. *p*-Sulphobenzeneazo-*m*-ethoxyphenol, flat, brownish-orange needles, with $1\text{H}_2\text{O}$, or a brick-red powder when dried, is obtained from resorcinol monoethyl ether and converted into 4-amino-5-ethoxyphenol (4-hydroxy-6-ethoxyaniline), grey, microscopic leaflets, m. p. 152—154°, 4-hydroxy-6-ethoxyacetanilide, pointed prisms, m. p. 172·5—174·5°, and the chloroacetanilide, feathery aggregates, m. p. 158·5—161°. 2:4-Dimethoxyaniline, m. p. 32·5—33·5°, is obtained from 4-hydroxy-2-methoxyacetanilide (compare Bechhold, A., 1889, 1155) and converted into 2:4-dimethoxychloroacetanilide, slender needles, m. p. 89·5—90° (corr.). The same compound is also ethylated, and thus made the source of 2-methoxy-4-ethoxyacetanilide, pale pink, glistening platelets, m. p. 117·5—118·5°. 2-methoxy-4-ethoxyaniline, faintly pink rhombs, m. p. 27·5—28·5° (corr.), b. p. 151·5—152·5°/12 mm., and the chloroacetanilide, flat, narrow, striated plates, m. p. 97·5—98°. The above 4-hydroxy-6-ethoxyacetanilide is methylated or ethylated, and converted in turn into 4-methoxy-6-ethoxyacetanilide, faintly pink, silky needles, m. p. 100·5—101°, 4-methoxy-6-ethoxyaniline, m. p. 22·5°, b. p. 144—144·5°, the chloroacetanilide, m. p. 126—127°, 2:4-diethoxyacetanilide, 2:4-diethoxyaniline, m. p. 33·5—34° (Will and Pukall, A., 1887, 660), and 2:4-diethoxychloroacetanilide, woolly needles, m. p. 102—103° respectively.

J. C. W.

Nitro-compounds for Use in Explosives. C. M. STINE (U.S. Pat. 1309551).—Dinitroxylylene nitrate,

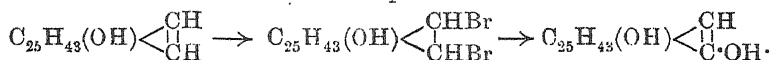


is produced by chlorinating xylene at 100° in sunlight until an increase in weight corresponding with the formation of the dichloro-derivative has been attained, cooling the reaction mixture to obtain a mass of crystals of *p*-xylylene chloride, and, after filtration, nitrating them with a mixture of nitric and sulphuric acids until a dinitro-derivative is obtained; this is heated with water under a pressure of 20 lb. per sq. in. until the chlorine has been replaced by the hydroxyl group, then evaporating the aqueous solution to expel water and hydrochloric acid, and obtain dinitro-*p*-xylylene hydroxide in well-defined crystals which are further nitrated. The

final product is a white, crystalline substance, which is stable and constitutes a powerful explosive. The following substances are also mentioned as capable of similar production and use: *dinitroxyglyl nitrate*, *nitrohydroxyxylylene nitrate*, *dinitrohydroxyxylylene nitrate*, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_3$, $\text{C}_6\text{HMe}(\text{NO}_2)_2(\text{CH}_2 \cdot \text{O} \cdot \text{NO}_2)_2$.

CHEMICAL ABSTRACTS.

Hydroxycholesterol. III. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1919, 106, 271—296. Compare A., 1914, i, 683; 1916, i, 558).—Cholesterol dibromide, prepared by brominating cholesterol, gives up a part of its bromine on heating with acetic acid. The bromine is removed from the dibromide more readily by boiling with water. By boiling for some time in the presence of sodium acetate in a reflux condenser it may be removed entirely, giving rise to a mixture which is partly amorphous and partly crystalline. The spectrum analysis and other reactions show that the amorphous product is hydroxycholesterol, identical with the compound obtained by the oxidation of cholesterol. The formation of hydroxycholesterol from the dibromide of cholesterol is represented as follows:



The double bond of the cholesterol eliminated by the bromination is thus re-established.

The crystalline substance, m. p. 139—141°, is a modified cholesterol, for which the author proposes the name of *metacholesterol*. A similar substance is prepared directly from cholesterol by oxidation. Mineral acids have the same effect on cholesterol dibromide as water, only the reaction is more vigorous.

On boiling cholesterol dibromide with dilute aqueous potassium hydroxide, hydroxycholesterol as well as the unchanged dibromide is obtained. Alcoholic potash, on the other hand, produces a substance which shows the properties of a hydroxy-derivative of cholesterol, but is not identical in its properties with the known hydroxycholesterol. The author names this substance *isohydroxycholesterol*. Details are further given of the bromination of hydroxycholesterol.

S. S. Z.

Crystallography of Phenyl Benzoate. MARIA STURA (*Riv. Min. Crist. Ital.*, 1917, 48, 86—90).—This compound is monoclinic; complete crystallographic data are given. CHEMICAL ABSTRACTS.

Action of Cyanogen Bromide on Aromatic Hydrocarbons under the Influence of Aluminium Chloride. P. KARRER and E. ZELLER (*Helv. Chim. Acta*, 1919, 2, 482—486).—When aromatic hydrocarbons are mixed with finely powdered aluminium chloride and freshly prepared cyanogen bromide and subsequently warmed until evolution of halogen hydrides ceases, good yields of nitriles are obtained. Toluene gives *p*-toluonitrile with a very little of the *o*-nitrile, and anthracene, dissolved in carbon disulphide, gives the unknown *anthracene-9-carboxylonitrile*, m. p. 170—172°, which is

identified by hydrolysis to the known acid and oxidation to anthraquinone.

Scholl and Nörr obtained quite different results when investigating this reaction (A., 1900, i, 386). It may be that they did not use fresh cyanogen bromide, for this is essential to the production of nitriles.

J. C. W.

Preparation of Vanillin. CONFECTIONERY INGREDIENTS, LTD., FRANCIS EDWARD MATTHEWS, ALBERT THEODORE KING, and THOMAS KANE (Brit. Pat., 131161).—Acyl derivatives of 4-hydroxy-3-methoxybenzoyl chloride, such as the acetate, benzoate, or carbonic ester or the *p*-toluenesulphonic ester, and arylalkyl derivatives, such as the benzyl ether, are reduced to the corresponding vanillin derivatives when their solution in toluene, xylene, or other suitable inert solvent is subjected at boiling temperature to a current of dry hydrogen in presence of a suitable catalyst; this may consist of any metal ordinarily known to be suitable for carrying out hydrogenations or reductions in liquid media (although palladium is preferred), deposited if desired on asbestos or barium sulphate or other suitable carrier. The product of reduction is hydrolysed to vanillin. Thus a nearly theoretical yield of vanillin sodium hydrogen sulphite is obtained when dry hydrogen is passed through a boiling mixture of vanilloyl chloride *p*-toluenesulphonic ester (154 parts), dry xylene (1000 parts), and palladised barium sulphate (5%, 30 parts) until evolution of hydrogen chloride ceases.

H. W.

Benzaldoxime Peroxide. PAUL ROBIN (*Compt. rend.*, 1919, 169, 695—696).—Contrary to Beckmann's results (compare A., 1889, 980), the author finds that when benzaldoxime peroxide is boiled in benzene it decomposes, giving benzaldoxime and dibenz-enyloxyazoxime. When oxidised by iodine and sodium carbonate the peroxide gives dibenzenyloxyazoxime and its decomposition products.

W. G.

Hydroxy-carbonyl Compounds. II. Synthetic Experiments in the Filix Group. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 466—481. Compare this vol., i, 160).—The extract of male fern root (*Aspidium filix mas*), which is the favourite remedy against the tape-worm, contains a number of active principles which have been investigated by Boehm (A., 1898, i, 40; 1899, i, 32, 804; 1902, i, 36, 37). These are all butyryl derivatives of phloroglucinol ethers, aspidinol having one benzene nucleus, albaspidin and flavaspidic acid having the structure of diphenylmethane, and filixic acid that of triphenylmethane. With the exception of the alkaloids of the pomegranate root, all other known tænia drugs are also butyric or isobutyric acid derivatives. It is, therefore, of interest to synthesise simple butyrophenones in order to test their physiological action. In addition, many indications have been received that the activity of related substances is greater the fewer the number of methyl

groups which are present as substituents in the nuclei. For example, tryptaflavine is more active than acridine-yellow, salvarsan than its dimethyl derivative, and cignolin than chrysarobin. Consequently, the aim in the present synthesis is to obtain butyrophenone derivatives with as few methyl groups as possible. Hoesch's method has again proved successful, the butyronitriles condensing quite readily with phloroglucinol derivatives in the presence of hydrogen chloride and zinc chloride.

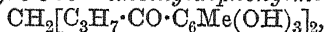
Phlorobutyrophenone [2:4:6-trihydroxyphenyl propyl ketone] crystallises in long needles with $1\text{H}_2\text{O}$, which lose water at 110° and then have m. p. $179\text{--}180^\circ$. It gives an intense red colour with ferric chloride, and couples with diazoaminobenzene to form 2:4:6-trihydroxy-3:5-dibenzeneazophenyl propyl ketone, in felted masses of orange-red needles, m. p. $136\text{--}137^\circ$. *Phloroisobutyrophenone* [2:4:6-trihydroxyphenyl isopropyl ketone] also crystallises with $1\text{H}_2\text{O}$ in white needles, m. p. $177\text{--}178^\circ$ (mixed m. p. 174°).

Methylphloroglucinol is prepared by dissolving phloroglucinol in water, adding hydrochloric acid and formalin, and reducing the precipitate of hexahydroxydiphenylmethane with zinc dust and sodium hydroxide. It reacts as above to form *methylphlorobutyrophenone* [2:4:6-trihydroxy-m-tolyl propyl ketone], which crystallises with $1\text{H}_2\text{O}$, m. p. $154\text{--}155^\circ$, and gives a violet colour with ferric chloride. Dimethylphloroglucinol yields *dimethylphlorobutyrophenone* (2:4:6-trihydroxy-m-5-xylyl propyl ketone), which is less soluble than the isomerides, crystallises in anhydrous, felted needles, m. p. 140° , and gives a dirty, yellowish-brown colour with ferric chloride.

Phloroglucinol monomethyl ether gives the two isomeric phlorobutyrophenone methyl ethers. One is more soluble in light petroleum and less soluble in water than the other, and these are sufficient reasons for supposing that this one has the ketone group opposite the methoxyl group, that is, it is 2:6-dihydroxy-4-methoxyphenyl propyl ketone; it crystallises in pale yellow leaflets, m. p. 113° . The isomeride, 2:4-dihydroxy-6-methoxyphenyl propyl ketone forms pure white needles, m. p. 130° .

Methylphloroglucinol *p*-methyl ether yields 2:4-dihydroxy-6-methoxy-m-tolyl propyl ketone, in white needles, m. p. 151.5° . Aspidinol, m. p. $156\text{--}160^\circ$, is the 4:6-dihydroxy-2-methoxy-derivative, and therefore the synthetic ketone is designated *isoaspidinol*.

Methylphlorobutyrophenone condenses with formaldehyde in the presence of dilute sodium hydroxide to form 2:4:6:2':4':6'-hexahydroxy-5:5'-dibutyro-3:3'-dimethyldiphenylmethane,



which crystallises in microscopic needles, m. p. 212° . Phlorobutyrophenone and phloroisobutyrophenone also condense with formaldehyde to form such compounds, but owing to the free position in the nuclei, further condensations take place to a certain extent and the products are impure.

The naturally occurring filix compounds are more active the more complex they are, but of the above synthetic products the unicyclic ones are more active than the diphenylmethane representatives.

Phloroisobutyrophenone, which so closely resembles its isomeride in m. p. and chemical properties, has about twice its activity.

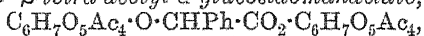
J. C. W.

Hydroxy-carbonyl Compounds. III. Synthesis of iso-Cotoin. P. KARRER (*Helv. Chim. Acta*, 1919, 2, 486—489).—With the hope of synthesising cotoin (2:6-dihydroxy-4-methoxybenzophenone), the active ingredient of coto-bark, Hoesch's method has been applied to phloroglucinol monomethyl ether and benzonitrile. The only product which could be isolated, however, and this in good yield, is isocotoin [2:4-dihydroxy-6-methoxybenzophenone], which crystallises from water in yellow needles, m. p. 162° (cotoin has m. p. 131°). It seems to be the rule that ketones of this type, with the methoxyl group adjacent to the ketone group, are more soluble in water and less soluble in light petroleum than their isomerides with a *p*-methoxyl group [compare paeonol and isopaeonol, acetovernone and isoacetovernone (A., 1915, i, 820), and the phlorobutyrophenone methyl ethers (preceding abstract)].

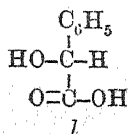
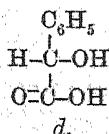
Piperonylonitrile forms a double compound with zinc chloride, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CN}\cdot\text{ZnCl}_2$, which crystallises in slender needles, m. p. 157—158°, and therefore cannot be used in Hoesch's synthesis.

J. C. W.

Glucosides. IV. The Glucosides of Mandelic, Lactic, and Salicylic Acids. A New Chemical Resolution of Mandelic Acid. P. KARRER, C. NÄGELI, and H. WEIDMANN (*Helv. Chim. Acta*, 1919, 2, 425—436. Compare this vol., i, 338).—Besides the tetra-acetylglucosidomandelic acids and the tetra-acetylglucose mandelates which are formed when the silver salts of active and inactive mandelic acids are treated with acetobromoglucose, *l*-mandelic acid, and this isomeride only, gives a tetra-acetyl-*d*-glucose β -tetra-acetyl-*d*-glucosidomandellate,



in snowy crystals, m. p. 235°, $[\alpha]_D^{25} -74.96^\circ$ (in chloroform). A separation of the three products is effected as follows. The tetra-acetylglucosidomandellate remains in solution in the toluene on cooling the reaction mixture, whilst the new ester and the tetra-acetylglucose mandellate separate. The new ester is almost insoluble in alcohol, and may thus be freed from the tetra-acetylglucose mandellate. Starting with inactive mandelic acid, a clear separation of the active components may thus be effected. The different behaviour of the two acids may be explained on steric grounds; it is possible that in the *d*-acid the hydroxyl groups are so near together that there is only room for one tetra-acetylglucose residue at a time, thus:



If this is so, then inactive acetobromoglucose should effect the same separation, and the authors are collecting the necessary material for such an investigation.

More complete directions are given for the preparation, from the tetra-acetyl compounds, of β -*d*-glucosido-*d*- and -*l*-mandelic acids. These crystallise with 1EtOH in slender needles. β -*d*-Glucosido-*dl*-lactic acid, a hygroscopic, snowy powder, is also more completely described.

Tetra-acetyl-*d*-glucose salicylate has $[\alpha]_D^{16} - 39.50^\circ$ (in chloroform) and β -tetra-acetyl-*d*-glucosidosalicylic acid has $[\alpha]_D^{16} - 28.47^\circ$ (compare A., 1917, i, 539). The latter has now been hydrolysed to β -*d*-glucosidosalicylic acid, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CO_2H$, which crystallises in radiate bundles of needles with $1H_2O$, m. p. 142° (decomp.), $[\alpha]_D^{16} - 49.25^\circ$, and may be called *salicinic acid*, because of its relationship to salicin.

J. C. W.

A Simple Method of Demonstrating the Production of Aldehyde by Chlorophyll and by Aniline Dyes in the Presence of Sunlight. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, 5, 511—513).—For the preparation of chlorophyll for the experiments described, fresh leaves were extracted with alcohol, the alcoholic extract shaken with carbon tetrachloride, and the carbon tetrachloride, after separation, sprayed on to filter paper and allowed to evaporate. After spraying the paper several times, it acquired a deep green colour. A bell jar was lined with such filter paper, moistened with water, and then inverted over a small dish of water, sealed from the air and exposed to sunlight. When the paper was bleached to a pale green colour, the water in the dish generally gave a positive test for aldehydes, indicating the formation of a volatile aldehyde. The result was the same whether carbon dioxide was entirely excluded from the air in the jar or whether its concentration was increased to 10%. This supports the view that the aldehyde is not produced by the decomposition of carbon dioxide, but rather by the decomposition of the chlorophyll.

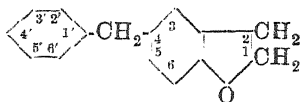
Similar results were obtained when a number of aniline dyes, particularly methyl-green and iodine-green, were used in place of chlorophyll.

W. G.

Syntheses in the Catechin Group. P. KARRER and FR. WIDMER (*Helv. Chim. Acta*, 1919, 2, 454—465).—Compounds of the type of catechin, $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H(OH)_2 \leftarrow \begin{array}{c} CH_2 \cdot CH_2 \\ | \\ O \end{array}$,

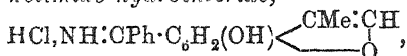
are widely distributed in nature, but the only syntheses which have been effected in this series are due to Kostanecki and his pupils; they are very complicated, and so far have only furnished methyl ethers of the desired products. A simple method has now been discovered. Hydroxycoumarones or hydroxycoumarans are condensed with nitriles under the influence of hydrogen chloride, and the ketimides so formed are boiled with water, giving ketones which are easily reduced to the required secondary alcohols. The method is, in effect, another application of Hoesch's synthesis of phenolic ketones (A., 1915, i, 820; 1917, i, 342).

It is proposed to call the parent 4-benzylcoumaran "depsan," and the coumarone derivative "depsen," with depsanone and depsenone for the ketones, and depsanol and depsenol for the secondary alcohols, the notation being as in the annexed formula.



Resorcinol and ethyl chloroacetate are condensed in the presence of sodium ethoxide to ethyl *m*-hydroxymethylcoumarilate, m. p. 178°, which is hydrolysed to the free acid, m. p. 226° (evolution of carbon dioxide). The dry acid is heated at 180—190°, when 5-hydroxy-2-methylcoumarone is obtained as a sublimate of white needles, m. p. 103°, which may be preserved for a long time. This mode of preparation is an improvement on that of Hantzsch (A., 1887, 262) or Pechmann (A., 1901, i, 211). The coumarone exhibits sky-blue fluorescence in alkaline solutions, and gives a brownish-red coloration with alcoholic ferric chloride, which changes to blue on diluting with water. By reduction with sodium and alcohol, it yields 5-hydroxy-2-methylcoumaran, $\text{OH} \cdot \text{C}_6\text{H}_3 \text{---} \text{CHMe} \cdot \text{CH}_2$, which sublimes or crystallises in white needles, m. p. 96°.

5-Hydroxy-2-methylcoumarone is dissolved in ether, mixed with a little zinc chloride and an equivalent quantity of benzonitrile, and the whole submitted to a current of dry hydrogen chloride for six hours. The *ketimide hydrochloride*,



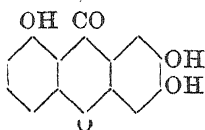
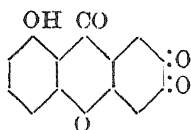
which separates in bundles of pale green crystals, m. p. 77°, is boiled with water, and thus hydrolysed to 5-hydroxy-2-methyldepsenone (5-hydroxy-4-benzoyl-2-methylcoumarone). This crystallises in slender, golden-yellow forms, m. p. 158°, gives an intensely yellow sodium salt, and may be methylated by methyl sulphate. 5-Methoxy-2-methyldepsenone forms stout, pale yellow crystals, m. p. 79°, and does not reduce permanganate. This is important, as it shows that the furan ring of the original coumarone has not been ruptured during the condensation with the nitrile. Reduction of the ketone to the hydrol is effected by zinc dust and 5% sodium hydroxide. 5-Hydroxy-2-methyldepsenol forms bundles of small, very pale pink crystals, m. p. 141°.

5-Hydroxy-2-methyldepsanone, small, sulphur-yellow needles, m. p. 159°, giving a green coloration with alcoholic ferric chloride, and 5-hydroxy-2-methyldepsanol, slender, pale pink needles, m. p. 152° (turns dark brownish-red at 100°), are obtained in the same way from 5-hydroxy-2-methylcoumaran. J. C. W.

Correction of an Error Relating to a Trihydroxyxanthone.

A. L. VAN SCHERPENBERG (*Chem. Weekblad*, 1919, 16, 1146—1149). —When euxanthone is oxidised with chromic acid, a red substance is obtained to which the constitution 2-hydroxy-5:8-quinoxanthone has been assigned (Nierenstein, A., 1913, ii, 382). Reduction of

this compound with zinc in acetic acid gives a yellow substance of the corresponding structure, 2:5:8-trihydroxyxanthone. The following arguments, based on the experimental results of Nierenstein, are advanced by the author against the adoption of this view. The red substance, on treatment with nitric acid, gives trinitroresorcinol, indicating the presence of a resorcinol residue not accounted for by the above formulation. Attempts to acetylate, benzoylate, and alkylate the quinone substance were not successful. This accords with the view that the hydroxyl group occupies the 8-position, and not the 3-position. The yellow reduction product melts with decomposition, a property of hydroxyxanthones with a hydroxyl group in the 3- or 6-position. The formulation of the two substances as 8-hydroxy-2:3-quinoxanthone and 2:3:8-trihydroxyxanthone, respectively, is therefore proposed.



W. S. M.

δ -Cinchonine and its Isomerides ; its Relations to Niquine.

E. LÉGER (*Compt. rend.*, 1919, **169**, 797—800).—By fractional crystallisation of its hydrochloride from alcohol, it is now shown that the δ -cinchonine previously described by Jungfleisch and Léger (compare A., 1894, i, 262) is really a mixture of two isomerides, which the author names α -cinchonhydrine and β -cinchonhydrine. These substances have respectively m. p. 144.4° and 155.8° , $[\alpha]_D +196.8^\circ$ and $+106^\circ$ (in water with 2HCl), $[\alpha]_D +139.8^\circ$ and $+72.16^\circ$ (in alcohol). These figures indicate that the δ -cinchonine described by Langer (compare A., 1901, i, 403) is identical with the α -cinchonhydrine now described. With each of these bases, acetic anhydride gives a diacetyl derivative, from which the original base can be regenerated unchanged.

When heated for twenty-four hours with 50% sulphuric acid, α -cinchonhydrine is converted into γ -cinchonhydrine, which has $[\alpha]_D +140.2^\circ$.

It is suggested that the cinchonhydrines bear the same relationship to cinchonine as niquine does to hydroquinine. W. G.

The Crystallography of Morphine and certain of its Derivatives. EDGAR T. WHERRY and ELIAS YANOVSKY (*J. Washington Acad. Sci.*, 1919, **9**, 505—513).—Attempts have been made to apply the optical-crystallographic method devised for the identification of the cinchona alkaloids (A., 1918, ii, 339) to the morphine group of alkaloids and the crystallographic and optical properties of a number of these have been studied. Owing to the ready solubility, however, of these substances in every immersion liquid approaching them in refractive index, the method is impracticable.

Morphine monohydrate, $C_{17}H_{19}O_3N \cdot H_2O$, was obtained in good crystals from methyl alcohol: rhombic bisphenoidal [$a:b:c=0.499:1.0:0.927$]; refractive indices, α 1.580, β 1.625, γ 1.645. D 1.32; M.V. 229.7.

Codeine (morphine methyl ester), $C_{18}H_{21}O_3N$, was crystallised from ethyl acetate: rhombic bisphenoidal [$a:b:c=0.931:1.0:0.509$]; double refraction positive, dispersion strong. D 1.32; M.V. 226.7.

Codeine monohydrate, $C_{18}H_{21}O_3N \cdot H_2O$, was crystallised from water and from aqueous methyl alcohol: rhombic, probably bisphenoidal [$a:b:c=0.960:1.0:0.830$]; double refraction negative, dispersion distinct. D 1.31; M.V. 242.1.

Codethyline (morphine ethyl ester monohydrate), $C_{19}H_{23}O_3N \cdot H_2O$, crystallised from ether in prisms: rhombic, probably bisphenoidal [$a:b:c=1.454:1.0:0.789$]; double refraction positive, dispersion distinct. D 1.29; M.V. 256.7.

Heroine (diacetylmorphine), $C_{21}H_{23}O_5N$, was obtained in excellent crystals from ethyl acetate: rhombic bisphenoidal [$a:b:c=0.8952:1.0:0.497$]; double refraction negative, dispersion strong. D 1.32; M.V. 279.7.

The relations between the topic parameters of the crystals are discussed. E. H. R.

Addition Reactions and Ring Fission of certain Heterocyclic Compounds. SIEGFRIED SKRAUP (*Annalen*, 1919, **419**, 1—92).—The behaviour of various heterocyclic compounds towards hydroxylamine has been investigated; the results are interpreted with the aid of Werner's theory of the varying affinity values of simple bonds.

Ethyl 2:4:6-trimethyldihydropyridine-3:5-dicarboxylate reacts with hydroxylamine hydrochloride in boiling absolute methyl alcoholic solution to yield ammonium chloride, ethyl 2:4:6-trimethylpyridine-3:5-dicarboxylate, and 4-ethylidenbis-3-methyl-5-*isooxazolone*, $O \begin{array}{c} \diagup O \cdot \text{CH} - \text{CHMe} - \text{CH} \cdot \text{CO} \\ \diagdown \text{N} = \text{CMe} \quad \text{MeC} = \text{N} \end{array} O$, m. p. 156° (compare Rabe, A., 1904, i, 509). The primary product of the action appears to be ethyl ethylidenbisacetoacetate, which then yields the *isooxazolone* on the one hand and the pyridine derivative on the other hand through the intermediate formation of a *N*-hydroxy ring compound. In support of this hypothesis, it is found that small quantities of ethyl trimethylpyridinedicarboxylate are formed by the action of hydroxylamine hydrochloride on ethyl ethylidenbisacetoacetate. Under similar conditions, ethyl 2:6-dimethyldihydropyridine-3:5-dicarboxylate yields ethyl 2:6-dimethylpyridine-3:5-dicarboxylate in 20% yield, whilst a 49.5% yield of ethyl 4-phenyl-2:6-dimethylpyridinedicarboxylate, m. p. 66° (*picrate*, m. p. 148—149°), is obtained from the corresponding dihydro-compound. With ethyl 2:6-dimethylisopropylidihydropyridinecarboxylate and ethyl 4-benzyl-2:6-dimethyldihydropyridinedicarboxylate a different but not unexpected behaviour is observed, since in each case the substituting group is eliminated and ethyl 2:6-dimethylpyridinedicarboxylate is produced.

Ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate only reacts very slowly with hydroxylamine hydrochloride. The transformation of the dihydro-derivatives into the pyridine compounds can scarcely be ascribed to a direct oxidising action of hydroxylamine since, though these substances are readily oxidised by such agents as nitrous acid, sulphur, nitric and chromic acids, they are very resistant to iodine, ferric chloride in acetone solution, and to a large excess of permanganate.

A rigid proof of the relationship of dimethyldihydropyridine- and trimethyldihydropyridine-dicarboxylic esters to 1:4-dihydropyridine has not previously been given; attempts to identify the presence of an imino-hydrogen atom by acetylation were unsuccessful, but its presence could be shown with the help of magnesium methyl iodide.

Benzothiazole is transformed by hydroxylamine into 2-amino-benzothiazole, the yield being nearly quantitative; similarly, benzoxazole is converted into 2-aminobenzoxazole, m. p. 129—130°, and *o*-formylaminophenol (identified as dibenzoyl-*o*-aminophenol, m. p. 182—183°). The following substances do not react with hydroxylamine: benziminazole (the *picrate*, m. p. 225—226°; *copper salt*, $(C_7H_5N_2)_2Cu$, red precipitate; *nickel, cobalt, cadmium, and zinc* compounds are described); 1-methylbenziminazole (m. p. 66°, b. p. 286°/746 mm., conveniently prepared by the action of potassium methyl sulphate on sodium benziminazole in aqueous solution; *picrate*, m. p. 246—247°); 1-phenylbenziminazole, benzylidene-aniline, azobenzene, 1-phenylpyrazole, 2-phenyl-1:2:3-triazole, pyridine, quinoline, 2-methylbenzothiazole, 2-phenylbenzothiazole, 4:5-diphenyloxazole, 6-dimethylaminobenzothiazole.

The following 2-substituted benzoxazoles have been prepared by heating *o*-aminophenol with the requisite nitrile or amide: 2-*isobutyl*benzoxazole, almost colourless oil, b. p. 240°/748 mm., D^{17}_D 0.98; 2-*tert.-butyl*benzoxazole, colourless oil, b. p. 226°/748 mm., D^{17}_D 0.9466; 2-*n*-hexylbenzoxazole, b. p. 282—285°, m. p. 19°, D^{19}_D 0.944; 2-*cyclohexyl*benzoxazole, colourless crystals, m. p. 37—38°, b. p. 298°/744 mm.; 2-*benzyl*benzoxazole, pale yellow, viscous liquid, b. p. 325°/750 mm., D^{17}_D 1.113; 2-phenylbenzoxazole, non-fluorescent crystals, m. p. 103°; 2-*p*-tolylbenzoxazole, colourless needles, m. p. 116—117°; 2-*p*-anisylbenzoxazole, almost colourless, crystalline needles, m. p. 101°, b. p. 363°/742 mm.; 2-*a*-naphthylbenzoxazole, colourless crystals, m. p. 107°; 2-*p*-chlorophenylbenzoxazole, long, shining needles, m. p. 150°; 2-*p*-bromophenylbenzoxazole, m. p. 158—159°; 2-*styryl*benzoxazole (?). The fission of the oxazole ring by aqueous hydrochloric acid has been studied, and reaction is shown to occur with decreasing rapidity when the substituents are arranged in the following order: benzyl, methyl, *n*-hexyl, cyclohexyl, isobutyl, *tert*-butyl, phenyl, *p*-tolyl, *a*-naphthyl, *p*-anisyl. The results are fully discussed in the light of the theory of partial valency.

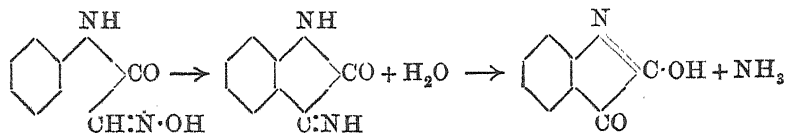
H. W.

Preparation of Isatin and its Substitution Derivatives and Intermediate Products. J. R. GEIGY (Brit. Pat. 128122).—The preparation of oximinoacetanilide and its substitution products

b b*

is effected by subjecting aniline or its derivatives which are substituted in the benzene nucleus by halogens, alkyl, alkoxy, or carboxyl groups or the *N*-monoalkyl or *N*-monoaralkyl derivatives of these amines to the action of chloral hydrate in a dilute solution of a mineral acid and in the presence of hydroxylamine at a suitable temperature. Isatin and its substitution derivatives are obtained from oximinoacetanilide and its derivatives by treatment of the latter with concentrated sulphuric acid and afterwards splitting the resulting isatinimides by addition of water into isatins and ammonia. Reactions occur in accordance with the schemes

$$\text{CCl}_3 \cdot \text{CH}(\text{OH})_2 + \text{NH}_2 \cdot \text{OH} = \text{CCl}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + 2\text{H}_2\text{O};$$

$$\text{CCl}_3 \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + \text{C}_6\text{H}_5 \cdot \text{NH}_2 + \text{H}_2\text{O} = \text{NHPh} \cdot \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{OH} + 3\text{HCl}.$$


Oximino-derivatives of the following amines have been prepared, the m. p.'s of the compounds being placed within brackets: *o*-toluidine (121°), *m*-toluidine (146°), *p*-toluidine (162°), *m*-xylidine (161°), *p*-xylidine (151°), methylaniline (145°), ethylaniline (160°), benzylaniline (142°), *o*-anisidine (140°), *p*-phenetidine (195°), anthranilic acid (208°), *o*-chloroaniline (150°), *m*-chloroaniline (154°), 2:5-dichloroaniline (163°), 3:4-dichloroaniline (158°), 3:5-dichloroaniline (185°), 5-chloro-*o*-toluidine (167°), 4-chloro-*o*-toluidine (148°), 6-chloro-*m*-toluidine (187°), 4-chloro-*m*-toluidine (134°), 2-chloro-*p*-toluidine (177°), 3-chloro-*p*-toluidine (188°), and *p*-bromoaniline (167°). The following isatins are described: mixture of 4- and 6-methylisatins, orange-yellow crystals, m. p. 143°; 4:7-dimethylisatin, orange-yellow crystals, m. p. 250°; 5:7-dimethylisatin, brick-red crystals, m. p. 235°; mixture of 4- and 6-chloroisatins, orange-yellow crystals, m. p. 212°; 7-chloroisatin, reddish-brown crystals, m. p. 175°; mixture of 4:5- and 5:6-dichloroisatins, yellowish-red crystals, m. p. 200°; 4:6-dichloroisatin, lemon-yellow crystals, m. p. 250°; 4-chloro-7-methylisatin, orange-yellow crystals, m. p. 273°; 5-chloro-7-methylisatin, yellowish-brown crystals, m. p. 265°; 7-chloro-4-methylisatin, orange-yellow crystals, m. p. 252°; mixture of 5-chloro-4-methyl- and 5-chloro-6-methylisatins, orange-yellow crystals, m. p. 200°; mixture of 4-chloro-5-methyl- and 6-chloro-5-methylisatin, bright red crystals, m. p. 205°; isatin-7-carboxylic acid, brownish-yellow powder, m. p. 235°. H. W.

Manufacture of *N*-Arylthiomorpholines. ROBERT ROBINSON, FRANCIS WILLIAM KAY, and BRITISH DYES, LTD. (Brit. Pat. 133108).—*N*-Arylthiomorpholines (*N*-arylthiazans) of the general formula $\text{Ar} \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{S}$, applicable as intermediate products in the manufacture of dyes, may be prepared by condensing primary aromatic amines, provided they are not substituted in the ortho-position, with $\beta\beta'$ -dichloroethyl sulphide. Suitable sol-

vents, such as toluene or nitrobenzene, may be employed, and also some agent capable of neutralising hydrogen chloride, such as sodium carbonate or acetate. In some cases, as in the reaction with β -naphthylamine, copper powder may be added with advantage. A less suitable method consists in heating the base and its hydrochloride with $\beta\beta'$ -dihydroxyethyl sulphide. *N*-Phenylthiomorpholine forms flat, elongated prisms, m. p. 32° , b. p. $200^\circ/50$ mm., has an alliaceous odour, and yields a *picrate*, m. p. 144° . *N*-*p*-Tolylthiomorpholine has m. p. 35° , and the β -naphthyl derivative has m. p. about 155° . J. C. W.

Ureides of Substituted Aminonaphtholsulphonic Acids.

B. HEYMANN, O. DRESSEL, R. KOTHE, and A. OSSENBECK (U.S. Pat. 1308071).—Ureides are produced having the general formula $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_m\text{Y}_4 - m\cdot\text{R}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_n\text{X}_6 - n\cdot\text{OH})_2$, in which R stands for a bivalent group containing an acyl radicle, for example, CO , SO_2 , $\text{CO}\cdot\text{CH}\cdot\text{CH}$, $\text{CO}\cdot\text{CH}_2$, or the residue of phenylacetic acid; n is the number of hydrogen atoms remaining unsubstituted in the naphthalene ring; X is a sulphonic acid or other substituting group; m the number of unsubstituted hydrogen atoms in the benzene nucleus; and Y, substituting atoms or radicles, such as Cl, Br, Me, or OMe. These compounds form dyes when coupled with diazotised aniline or similar components, and may be employed as therapeutic agents for destroying blood-parasites. They form salts with alkali metals, alkaline earth metals, or heavy metals, for example, sodium, barium, strontium, copper, zinc, mercury, and silver, which also possess therapeutic properties. As starting materials, 1:8-aminonaphtholsulphonic acids (mono-, di-, or higher sulphonic acids) may be employed. These compounds are substituted by such nitro-compounds as *p*-nitrobenzoyl chloride, *m*-nitroanisoyl chloride, *m*-nitrobenzenesulphonyl chloride, or *m*-nitrocinnamoyl chloride. Reduction of these substituted aminonaphtholsulphonic acids is effected by the action of iron and acetic acid or other similar reducing agents, and the amino-compounds thus obtained are treated with carbonyl chloride to obtain ureides. CHEMICAL ABSTRACTS.

Hydrazino-acids. III. AUGUST DARAPSKY (*J. pr. Chem.*, 1919, [ii], 99, 179—231. Compare A., 1918, i, 506, 553).—The hydrazino-acids described previously have been optically inactive; the author now describes the preparation of the optically active α -hydrazinophenylacetic acids, which are prepared by the action of hydrazine hydrate on the active phenylchloroacetic acids or by the resolution of α -benzylidenehydrazinophenylacetic acid and subsequent elimination of the benzylidene group. The applicability of these acids to the study of the phenomena of the Walden inversion is limited by their tendency to complete racemisation under the experimental conditions adopted.

d- and *l*-Phenylchloroacetic acids are prepared by the resolution of the *r*-acid by means of morphine according to the method of McKenzie and Clough (T., 1908, 93, 817; 1909, 95, 782), and their properties agree completely with those given by these authors; the unusual experimental difficulties encountered in this resolution have

been extensively investigated, the main factors conditioning success appearing to be the slowness with which the crystals of the salt separate and the relative weight of the crop which is deposited before filtration. *d-Hydrazinophenylacetic acid* is obtained by the action of hydrazine hydrate on *l*-phenylchloroacetic acid in absolute alcoholic solution; it crystallises in shining leaflets, m. p. 183—184°, and has $[\alpha]_D^{20} + 158.02^\circ$ in *N*-hydrochloric acid solution; *l-hydrazinophenylacetic acid*, m. p. 183—184°, $[\alpha]_D^{20} - 157.64^\circ$, is similarly prepared from the *d*-chloro-acid. The acids readily condense with benzaldehyde in aqueous solution in the presence of hydrochloric acid, yielding respectively *d*- and *l*-benzylidenehydrazinophenylacetic acids, m. p. 136—138°, $[\alpha]_D^{20} + 166.40^\circ$ and -166.59° in acetone solution.

The resolution of α -hydrazinophenylacetic acid into its active components cannot be conveniently effected by means of helicine or camphor, but may be accomplished if the acidic character of the substance is increased by the introduction of suitable groups; the formyl and benzoyl groups are not applicable, since viscous syrups are formed in the first instance and difficultly decomposable compounds in the second. The benzylidene derivative can, however, be resolved by morphine in alcoholic solution. (The crystalline quinine salts of *dl*-benzylidenehydrazinophenylacetic, *dl*-*o*-hydroxybenzylidenehydrazinophenylacetic and *dl*-*p*-methoxybenzylidenehydrazinophenylacetic acids, m. p.'s 172—174°, 183°, and 161—163° respectively, are described, but are not suited for the resolution; *dl*-*p*-methoxybenzylidenehydrazinophenylacetic acid forms small, colourless needles, m. p. 131—133°.) The physical properties of the *d*-acid obtained in this manner agree completely with those of the substance prepared by the action of hydrazine hydrate on *l*-phenylchloroacetic acid and treatment of the product with benzaldehyde.

Ethyl d- and *l*-hydrazinophenylacetate hydrochlorides, prepared by the esterification of the corresponding acids with alcohol and hydrogen chloride, have m. p. 148—150°, $[\alpha]_D^{20} + 96.32^\circ$ and -96.30° respectively. They are converted by nitrous acid into the corresponding nitroso-esters of the same sign, but considerable racemisation occurs which appears to be attributable to the nitrous acid; this is the more remarkable since a group directly attached to the asymmetric carbon atom is not involved in the change; further extensive racemisation takes place when the crude nitroso-esters are crystallised from alcohol. On the other hand, the conversion of nitroso- into azido-ester by treatment with dilute sulphuric acid appears to occur without racemisation, and yields a product of the same sign, but it is not possible to guarantee the optical purity of these substances. When the active nitroso-esters are heated they are converted into ethyl *dl*-aminophenylacetate, racemisation being complete.

dl-Azidophenylacetic acid, m. p. 98—101° (Forster and Müller, T., 1910, 97, 138, give 98.5°), is conveniently prepared by the action of sodium azide on *r*-phenyl-chloro- or -bromo-acetic acid; when the reaction is applied to *d*-phenylchloroacetic acid, a levorotatory azido-acid is obtained, which, however, is not free from mandelic acid.

Attempts to resolve *dl*-azidophenylacetic acid by quinine, quinidine, or cinchonine were unsuccessful, but partial success was attained with brucine or morphine, but the specific rotations of the acids were so low that, although the results are concordant among themselves, it is probable that the resolution was incomplete. Esterification of the azido-acids showed that racemisation unexpectedly occurs during the process, the phenomenon being more marked with alcohol and sulphuric acid than with diazoethane. Similar instances of racemisation were encountered with the active phenylchloroacetic acids, but, in these cases, the more marked effect was caused by diazoethane. Ethyl *d*-phenylchloroacetate has b. p. $138^{\circ}/19$ mm., $[\alpha]_D^{20} +121.05^{\circ}$ in alcoholic solution, but is possibly not quite free from the racemic substance. The values observed for the *l*-isomeride were b. p. $136^{\circ}/13$ mm., $[\alpha]_D^{20} -108.45^{\circ}$.

d-Hydrazinophenylacetic acid is converted by chlorine into *r*-phenylchloroacetic acid; similarly, ethyl *l*-hydrazinophenylacetate hydrochloride is transformed into slightly laevorotatory ethyl phenylchloroacetate, which is not quite pure analytically. H. W.

Cause of and Remedy for certain Inaccuracies in Hausmann's Nitrogen Distribution Method. S. L. JODIDI and S. C. MOULTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1526—1531).—The distribution of nitrogen in casein, gelatin, and egg-albumin has been investigated. It is shown that the proportion of amide nitrogen obtained by Hausmann's method as modified by Osborne and Harris (*A.*, 1903, i, 585) is constant, and does not depend on the quantity of magnesia added to the distillation mixture. The percentage of nitrogen contained in the magnesium oxide precipitate is higher the greater the quantity of magnesium oxide employed in distillation. Conversely, the proportion of monoamino- and diamino-nitrogen is the smaller the larger the amount of magnesia used in distillation. In order to obtain uniform results and a minimum of "humin" nitrogen it is necessary to use the least possible amount of magnesia which is sufficient to render the substance to be distilled alkaline. In the case of plant and animal materials the uniform application of 1 gram of magnesia is satisfactory, whilst in the case of proteins 0.5 gram is sufficient. J. F. S.

Identity of Hordein and Bynin. HEINRICH LÜERS (*Biochem. Zeitsch.*, 1919, **96**, 117—133).—Hordein and bynin were submitted to an analysis by the Van Slyke method, and the results obtained from the two proteins were almost identical. The author, therefore, does not agree with Osborne that bynin, which is obtained from malt, is a different protein from the hordein of barley.

S. S. Z.

Guanylic Acid, its Preparation and Precipitability. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 249—259).—By treating nucleoprotein from the pancreas of cattle with sodium hydroxide and precipitating with 90% alcohol in the presence of ammonium chloride, the sodium salts of guanylic and another

nucleic acid are obtained. After the purification of this mixture, sodium guanylate is obtained by precipitation with sodium acetate in the cold. Sodium hydrogen guanylate, $C_{10}H_{13}O_8N_5PNa$, is prepared by dissolving the latter in ten parts of hot water and one part of glacial acetic acid, and precipitating, after quick cooling, with three volumes of alcohol. S. S. Z.

Urease and the Radiation Theory of Enzyme Action.

I. and II. H. P. BARENDRECHT (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, 21, 1126—1142, 1307—1322).—After a criticism of the hypothesis put forward by Van Slyke (A., 1914, i, 1181), the author puts forward a new hypothesis to explain enzyme action. An enzyme acts by radiation, and the enzyme particle contains the same molecule, which is liberated or acted on by this enzyme, in some active state. The radiation by which enzymes exert their action is due to the electrons forming part of the atoms, and is of the nature of electromagnetic induction. The radiation, by which urease acts on urea, originates from the enzyme molecule, and is able to exert its hydrolytic effect to a certain distance, probably very small. When the urease radiation strikes an urea molecule, it is absorbed. The amount of urea hydrolysed in unit time by an enzyme molecule would therefore be independent of the urea concentration if the other constituents of the solution had no power of absorption of this radiation. In addition to urea, the hydrogen ions are the only constituent which absorb the radiation in this hydrolysis. At constant temperature and constant hydrogen-ion concentration, the velocity of the reaction is given by $-dx = m(x/[x + nc]) \cdot dt$, in which x is the concentration of urea, c the concentration of hydrogen ions, and n the absorption coefficient of hydrogen ions, that of urea being taken as unity. The velocity constant m for a given temperature and H^+ ion concentration is proportional to the enzyme concentration only. If a is the initial urea concentration and $(a-x)/a = y$, then, after integration, $nc/0.434 \cdot \log(1/[1-y]) + ay = mt$. This theory is tested by experiments made on the hydrolysis of urea by extract of soja beans, and the theory generally confirmed.

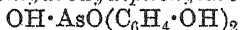
In the second paper, the work is repeated, but more precautions are taken to keep the hydrogen-ion concentration constant. It is found that the value of the constant m falls off towards the end of the reaction the higher the value of P_H . For low values of P_H , the value of m increases continually from 0.03% up to 8% urea concentration. For higher values of P_H , there is first an increase and then in the most concentrated solutions of urea a decrease in the value of m . These facts are deducible from the hypothesis formulated. J. F. S.

The Isomeric Hydroxyphenylarsinic Acids and the Direct Arsenation of Phenol. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1919, 41, 1440—1450).—By means of the diazo-reaction, *o*- and *m*-arsanilic acids (this vol., i, 50) have been converted into the phenolic acids. *o*-Hydroxyphenylarsinic

acid, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, crystallises readily from hot water, being but sparingly soluble in the cold, forming rosettes of needles, m. p. 196° , and its sodium salt, $\text{C}_6\text{H}_4\text{O}_4\text{AsNa}$, separates from 50% alcohol in glistening, hexagonal platelets with $4\text{H}_2\text{O}$. *m-Hydroxyphenylarsinic acid* crystallises from a small volume of water in masses of rhombs, m. p. $159\text{--}173^\circ$, and its sodium salt, rosettes of flat needles, is extremely soluble, even in alcohol. The ortho-acid differs from its isomerides in giving a wine-red colour with ferric chloride.

A knowledge of the *o*-hydroxyphenylarsinic acid has helped in the examination of the by-products formed in the arsenation of phenol. This important reaction is carried out as follows. Arsenic acid (480 grams of 80% acid), dehydrated by heating until the temperature reaches 150° , is mixed with phenol (200) and kept gently boiling at $155\text{--}160^\circ$ for seven hours. The homogeneous product is then diluted with water (2 litres), and sufficient of a hot concentrated solution of barium hydroxide is added to render the well-stirred mixture neutral to litmus. The precipitate of barium arsenate carries with it the small amount of tarry by-product. The hot filtrate is then treated with just sufficient sulphuric acid to precipitate the barium, filtered again, and the solution evaporated under reduced pressure to about half the volume, when it is neutralised by sodium hydroxide and concentrated to a small bulk. The hot solution is mixed with several volumes of alcohol and cooled, crystallisation being induced by rubbing. Using the quantities mentioned, about 120 grams of pure sodium *p*-hydroxyphenylarsinate are obtained, without the complications of Conant's method (this vol., i, 230).

The mother liquors, when the alcohol is removed by evaporation, give the above wine-red coloration with ferric chloride. Taking advantage of the different solubilities of the barium salts and the free acids, the authors have isolated *o*-hydroxyphenylarsinic acid (14 grams), Benda's *pp'*-dihydroxydiphenylarsinic acid, m. p. $250\text{--}251^\circ$ (10 grams; A., 1908, i, 747), and an acid which is probably *op'*-dihydroxydiphenylarsinic acid,



(8 grams). The latter acid crystallises from 50% acetic acid in stout, glistening prisms, m. p. $215\text{--}217^\circ$, and gives the red colour with ferric chloride.

J. C. W.

Physiological Chemistry.

Some Conditions Influencing the Reaction Velocity of Sodium Nitrite on Blood. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918—1919, 39, 149—156).—The rate of production of methæmoglobin by the action of sodium nitrite on blood is governed

by the nature and concentration of the blood solution and by the concentration of the sodium nitrite solution. Probably other factors, such as temperature, are of importance. J. C. D.

The Rôle of the Plasma Proteins in Diffusion. THOMAS HUGH MILROY and JOSEPH FRANCIS DONEGAN (*Biochem. J.*, 1919, **13**, 258—271).—After severe hæmorrhage, the specific gravity, viscosity, and percentage of nitrogen in the blood fall, whilst the conductivity rises. The fluid which enters the blood after hæmorrhage must have at least the electrolyte concentration of normal plasma, since there is no evidence of a fall in conductivity. It is evident from studies of diffusion of sodium chloride from solution in water, gum arabic solution, and blood serum that some factor other than viscosity is concerned in the diffusion of salt from serum. This point was studied further, and it is concluded from the results that the globulin may exert a determining factor governing the rate of diffusion. J. C. D.

Precipitation Structures Simulating Organic Growth. II. Physico-chemical Analysis of Growth and Heredity. R. S. LILLIE and E. N. JOHNSTON (*Biol. Bull.*, 1919, **36**, 225—273. Compare Lillie, A., 1918, i, 278).—If a piece of fine iron wire, wound round one end of a fine copper wire, is dropped into a 2% solution of egg-albumin containing 4% of potassium ferricyanide and 4% or more of sodium chloride, the entire surface of the iron wire rapidly becomes covered with fine, filamentous growths. They are characteristically regular in form; the majority are straight or slightly curved, and cease to grow at a length of 200 microns or less. A repetition of this experiment, using a 2% solution of egg-albumin containing 2% of potassium ferricyanide and 0.5% of sodium chloride, results in a slower growth, the form of the filaments is more irregular, and many larger structures are produced. In the stronger solution, growth usually ceases in about five minutes, whilst in the weaker solution it may continue for several hours. The action ceases when all the available potassium ferricyanide has been transformed, and may be renewed by adding more of the solution. The number of filaments may be limited by coating the metal with paraffin and removing the paraffin from very small areas before placing the metal in the solution. Experiments were made with iron, zinc, cobalt, cadmium, nickel, copper, lead, tin, chromium, and aluminium. For each metal which forms a precipitate with potassium ferricyanide there is a definite and characteristic type of precipitation structure. The presence or absence of a protective colloid has a marked influence on the kind of structure formed. Definite tubular filaments are produced from zinc, cadmium, and copper only in the presence of a protective colloid; in its absence, most of the precipitate appears "amorphous." Copper readily forms filaments in the absence of the protective colloid. The characters of structures produced with iron, zinc, cobalt, cadmium, copper, and nickel are described in detail. The form and rate of growth may be modified by the

passage of a weak electric current, by sudden changes in the concentration of the solution, and by the conditions of the surface of the metal, for example, whether rusty or not. All filaments are extremely sensitive to outside influences, such as jarring, causing currents, or addition of sand particles, any of which may cause change of direction of growth and change of form of filaments. Filaments grown on the surface show striking variations from those grown immersed. Certain metals, notably cadmium, show a rhythmic motion during growth. All these purely chemical and physical phenomena are significant in that they point the way to a better understanding of the phenomena of rhythm and periodicity in living beings.

CHEMICAL ABSTRACTS.

The Origin of Odour in the Molecules of Odoriferous Substances. HEINRICH TEUDT (*Prometheus*, 1919, 30, 201—204, 209—211; from *Chem. Zentr.*, 1919, iii, 138—139).—The author assumes that the origin of odour must be within the molecule, since the odour of a chemical compound is not, in general, affected by external influences as long as the molecule remains undecomposed. The source can scarcely lie within the atom, since, if this were so, every odoriferous atom must retain its odour in the free state and in combination with odourless atoms; the monatomic elements are, however, odourless, as are the ions of the strongly odoriferous halogens. The cause of the odour is to be sought between the atoms in the molecule which contain the valency electrons. It must be assumed that odours are caused by the vibrations of valency electrons, since the molecules of odoriferous substances are not altered in any way by the emission of odour. It appears probable that the nasal sensory nerves have electron vibrations which are increased by resonance when odoriferous particles having corresponding intramolecular electron vibrations are drawn into the nose in admixture with air. The author's investigations are explained by numerous diagrams. He is led to the conclusion that a chemical element can the more readily induce odour in its compounds in proportion as its electrons are more firmly united to the atomic nucleus. Metallic atoms, in consequence of the ease with which they detach electrons, are not suited to the production of odour. It can readily be seen that in all the horizontal series of the periodic system the power of giving odour increases as the metallic character of the element diminishes from left to right; correspondingly, the stability of the union between the atomic nucleus and the respective electrons increases from left to right. The author explains, further, the odourless or odoriferous character of certain substances, such as methane, ethane, the higher paraffins, carbon tetrachloride, etc., as well as the spread of odour to a distance and other phenomena.

H. W.

Place and Mode of Origin of the Acetone Substances. ERNST KERTESS (*Zeitsch. physiol. Chem.*, 1919, 106, 258—271).—Leucine was injected into the hind feet of dogs with an Eck's fistula and a "reverse" Eck's fistula. In the former case the injected sub-

stance is practically prevented from reaching the liver; in the second case, however, it does reach it. In the dogs with the "reverse" Eck's fistula, an increase in acetone, acetoacetic acid, and β -hydroxybutyric acid is recorded. The leucine does not alter the amount of excreted acetone substances in the dogs with Eck's fistula. The acetone substances, it is concluded, are therefore formed in the liver, and under certain physiological conditions they can be formed from leucine.

S. S. Z.

Chemical Studies in Physiology and Pathology. VIII. The Question as to Iodine Fixation in the Thyroid Gland.

E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1919, **96**, 260—269. Compare A., 1918, i, 47, 241, 355, 357; this vol, i, 297).—The juices of pig's thyroid, human serum, and milk were treated with potassium iodide and $N/10$ -iodine, and then precipitated with hot 90% alcohol. A repeated extraction of the coagula with boiling water removed practically all the iodine which was retained. No iodine was removed in this way from untreated coagulated juice of thyroid. The amount of iodine extracted from the juice of thyroid by means of alcohol depended on the water content of the alcohol. The author considers that these experiments support the theory which he discusses, that iodine is a component part of the protein molecule of the thyroid gland, and that it is not an essential constituent of the thyroid secretion.

S. S. Z.

Alleged Irreciprocal Permeability of the Frog's Skin to Ions. MARTIN GILDEMEISTER and JUSSUF SCHÜKRI (*Biochem. Zeitsch.*, 1919, **96**, 241—248).—The authors cannot confirm the results obtained by Bayliss (A., 1908, ii, 712) that the skin of the frog conducts electric currents in Ringer's solution better from the outside to the inside than in the reverse direction. They therefore do not accept the conclusion arrived at by Bayliss that the skin of the frog is permeable to sodium ions from the outside, but not from the inside.

S. S. Z.

The Diazo-reaction of Normal Human Urine and the Influence of the Mode of Nutrition on the "Diazo Value."

OTTO FÜRTH (*Biochem. Zeitsch.*, 1919, **96**, 269—297).—The diazo-chromogen of normal human urine was investigated. Utilising his simplified method of isolating the hydroxyproteic acids from urine by decomposing the urea with soja urease, the author prepared a "baryta fraction" from the acid contents of the urine. The "baryta fraction" was further fractionated with various precipitating reagents before and after hydrolysis and the various fractions were studied. The conclusion arrived at is that diazo-chromogen, although not identical with histidine, is, however, a closely related iminazole derivative. Probably it consists of one or more transformation or condensation products of histidine produced by intermediate metabolism. Diazo-chromogen has further been found to be thermostable, soluble in alcohol, insoluble in ether, and separated only with difficulty by means of acetone from the alcoholic solution. It does not give Millon's reaction.

Another part of this investigation was devoted to the study of the "diaz value" and the "diaz quotient" of the urine of normal subjects, tubercular subjects in the early stage of the disease, underfed subjects who subsisted on a diet deficient in protein, and cachectic individuals. From these observations and those made by Masslow the author concludes that the iminazole complex contained in the diazochromogen is of endogenous origin. S. S. Z.

Oxidation Procedure in the Human Organism. WALTER LASCH (*Biochem. Zeitsch.*, 1919, 97, 1—21).—As much as 12 grams per day of sodium thiosulphate can be consumed without harm. The thiosulphate is, however, not excreted as such in the urine, but is oxidised in the organism in accordance with the law observed by Tauber in the case of phenol. The ethereal sulphates increase slightly in the urine with intake of sodium thiosulphate. S. S. Z.

Origin and Significance of Acetoacetic Acid. L. C. MAILLARD (*Bull. Acad. med.*, 1919; from *J. Pharm. Chim.*, 1919, [vii], 20, 185—187).—A considerable quantity of acetoacetic acid was formed in a solution containing *cycloglycylglycine*, glycerol, and yeast-cells. The author suggests that the production of acetoacetic acid in the human body is due to the reduction of the dipeptide (removal of amino-groups), and not to an oxidising process. This conception appears to be more in harmony with the restricted oxidising faculty of diabetic subjects. W. P. S.

Preparation and Physiological Action of some Derivatives of Meconic Acid. L. LAUTENSCHLAGER (*Biochem. Zeitsch.*, 1919, 96, 73—86).—The following derivatives of meconic acid were synthesised and tested for their physiological action. *Acetyl* derivative, $\text{OAc}\cdot\text{C}_5\text{HO}_2(\text{CO}_2\text{H})_2$, forms colourless needles, m. p. 218° . The *benzoyl* derivative crystallises in colourless leaves, m. p. 248° (decomp.). The *methyl hydrogen* ester forms colourless crystals, m. p. 161.5° ; the *dimethyl* ester has m. p. 117° ; the *propyl hydrogen*, *dipropyl*, and *diisobutyl* esters form colourless crystals, m. p. 165° , 105° , and 98° respectively; the *diamyl* ester is a colourless oil. The *urethane* derivative forms colourless crystals, m. p. 124° .

Meconylcarbamide, $\text{CO} \begin{array}{c} \text{C(OH):C—CO—NH} \\ \text{CH=C—CO—NH} \end{array} \text{CO}$, forms a yellow powder, m. p. 173° (decomp.), and its *ethyl*, *propyl*, and *allyl ethers* are white, crystalline powders, m. p. 138° , 141° , and 143° (all decomp.) respectively. *Meconylthiocarbamide* is a clear, yellow, crystalline powder, m. p. 181° (decomp.), and its *propyl ether* has m. p. 138° (decomp.).

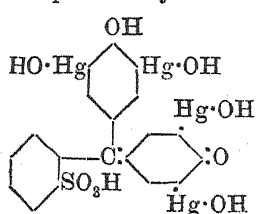
The acetyl and benzoyl derivatives and the aliphatic ethers of the acid produce, like the original acid, slight paralysis in the frog, but are inactive in the rabbit. The ethyl, and to a greater extent the propyl, ester produces a more marked action in the frog than the original acid. The corresponding monoalkyl derivatives are also

more active than the acid itself, but are not so potent as the normal esters. On the rabbit, however, this group of compounds produces no effect. The ether and diazo-compounds of the above esters behave physiologically like the esters themselves. The hydrazine derivative of meconic acid is very toxic and lethal in small doses.

The urethane derivative of meconic acid shows little potency, whilst the carbamide derivative is more active in the frog. The ethyl and propyl derivatives of the latter resemble meconic acid in their activity. Meconylthiocarbamide behaves like meconyl-carbamide, but is only one-third as potent. Its propyl derivative shows also some potency in the frog; in the rabbit the latter substances produce no effect. None of the synthesised substances has, therefore, manifested any definite narcotic action. S. S. Z.

Experimental Nephropathy produced by an Organo-mercury Compound of Phenolsulphonaphthalein. J. EDWARD BURNS, E. C. WHITE, and J. G. CHEETAM (*J. Urol.*, 1919, **3**, 1—16).

—As phenolsulphonaphthalein and mercury have special affinities for the secreting cells of the kidney it was thought that a compound containing these substances would attack these cells and not attack the other organs of the body, and the changes thereby produced would more nearly resemble the different types of nephritis found in the human being than those produced with other substances. The compound synthesised was tetrahydroxymercuriphenolsulphonaphthalein, which probably has the annexed



formula. It contains 63% of organically bound mercury. It is soluble in dilute alkali hydroxide. When given to dogs this substance produced acute and chronic renal lesions which resemble quite closely those found in the different types of nephritis in human beings. The lesions of the acute type were mainly tubular, although some slight glomerular changes were noticed. In the chronic type the most characteristic change is the increase of interstitial tissue both in the glomeruli and between the tubules, together with areas of tubular obliteration and glomerular fibrosis. Chemical examination of the blood and urine following the intravenous injection of sodium chloride and urea after the method of Underhill, Wells, and Goldschmidt (*J. Expt. Med.*, 1913, **28**, 322), showed results quite analogous to the type of lesion produced. This organo-mercury compound produced no lesions elsewhere in the body.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture

Comparative Studies on Respiration. VII. Respiration and Assimilation. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1919, 2, 1—3).—Certain improvements in technique are described; thus when a reagent is employed which has a “buffer” effect it is desirable to have the same “buffer” action during the measurement of normal respiration as during exposure to the reagent. An indicator should be present in the liquid containing the organisms, so that changes in reaction may be observed. Preliminary results indicate that there is pronounced antagonism between such substances as sodium chloride and calcium chloride in their effect on respiration.

J. C. D.

Comparative Studies on Respiration. VIII. The Respiration of *Bacillus subtilis* in Relation to Antagonism. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1919, 2, 5—15).—In relatively low concentrations of sodium, potassium, and calcium chloride the rate of respiration of *B. subtilis* remains fairly constant for a period of several hours, whilst in higher concentrations there is a gradual decrease in the rate. The effects of salts on respiration show a well-marked antagonism between sodium chloride and calcium chloride and between potassium chloride and calcium chloride. The antagonism between sodium and potassium chlorides is slight.

J. C. D.

Comparative Studies on Respiration. IX. The Effects of Antagonistic Salts on the Respiration of *Aspergillus niger*. F. G. GUSTAFSON (*J. Gen. Physiol.*, 1919, 2, 17—24).—In relatively dilute solutions sodium chloride and calcium chloride increase the respiration of *Aspergillus* in the presence of dextrose. Higher concentrations cause a decrease, probably due to the osmotic effects of the salts. The antagonism between sodium chloride and calcium chloride could be demonstrated by a study of the respiration of this organism. Spores germinated on a medium containing 0.5*M*-sodium chloride and 0.05% of dextrose, but failed to do so when calcium chloride was used instead of sodium chloride, or when both salts were present. Apparently a substance may have different effects on respiration from those which it has on growth. J. C. D.

Proteinogenous Amines. IV. The Production of Histamine from Histidine by *Bacillus coli communis*. KARL K. KOESSLER and MILTON T. HANKE (*J. Biol. Chem.*, 1919, 39, 539—584).—*Bacillus coli communis* does not form histamine from histidine when acting alone, in the presence of nitrates or ammonium salts, or in a medium containing glycerol. When glycerol or dextrose and a source of nitrogen, such as potassium nitrate or ammonium chloride, are present, some 50% of the histidine is con-

verted into histamine. Under these conditions the medium becomes acid, and the suggestion is advanced that histamine is produced by the bacillus as a means of neutralising the acid produced from glycerol. Contrary to many statements, it is found that histamine is never produced except in the presence of an easily available source of carbon.

J. C. D.

Formation of δ -Iminazolyl-lactic Acid from *l*-Histidine by Bacteria. K. HIRAI (*Act. Schol. Med. Kyoto*, 1919, 3, 49—53; from *Physiol. Abstr.*, 1919, 4, 256).—Histidine hydrochloride, prepared from ox blood, was acted on for forty days in protein-free nutrient media with a strain of *Proteus vulgaris* which was capable of converting *l*-tyrosine into γ -hydroxyphenyl-lactic acid. The product was separated by precipitation with phosphotungstic acid; it crystallised with $1\text{H}_2\text{O}$ and had $[\alpha]_D^{25} + 33.7^\circ$, the yield being 11%. It was identified by elementary analysis and by means of the platinichloride.

H. W.

Application of the Fixation Method in Bacterial Fermentation. I. Acetaldehyde as an Intermediate Product in the Fermentation of Sugar, Mannitol, and Glycerol by *Bacillus coli*, Dysentery, and Gas Gangrene Organisms. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, 96, 133—158).—By employing sodium sulphite and calcium sulphite as "fixing" agents, acetaldehyde has been established as an intermediate product in the fermentation of dextrose, mannitol, and glycerol. *B. coli* was employed in the fermentation of dextrose, Flexner Y and Shiga-Kruse cultures in the fermentation of mannitol and Fränkel's bacillus (*B. Welchii*) in the fermentation of glycerol. As the last-mentioned organism is an anaerobe the possibility of the formation of acetaldehyde as a secondary product from the alcohol produced is excluded.

S. S. Z.

Application of the Fixation Method in Bacterial Fermentation. II. The Establishment of an Aldehyde Stage in Acetic Acid Fermentation. C. NEUBERG and F. F. NORD (*Biochem. Zeitsch.*, 1919, 96, 158—175).—Alcohol was fermented in the presence of calcium sulphite with *Bacterium Orleanense*, *B. Ascendens*, and *B. Pasteurianum*. In each case acetaldehyde was established as an intermediate product in the fermentation.

S. S. Z.

Acid Fermentation of Xylose. E. B. FRED, W. H. PETERSON and AUDREY DAVENPORT (*J. Biol. Chem.*, 1919, 39, 347—383).—Xylose is readily fermented by bacteria which are found in fresh silage, sauerkraut, and manure, and also in certain soils, but the organisms commonly studied in the laboratory failed to break down the sugar. The organisms which can effect the fermentation are readily isolated in pure culture. The fermentation takes place either in the presence of free oxygen or in a limited supply, and the main products formed are acetic acid and lactic acid. The

relation of acetic acid to lactic acid approaches the theoretical ratio of 40 to 60 that would obtain if these two compounds were the only products arising from fission of the xylose molecule. Traces of carbon dioxide and ethyl alcohol were detected. Other sugars are fermented by these xylose-fermenting bacteria. J. C. D.

Mode of Action of Metal Sols. C. R. MARSHALL (*Proc. Roy. Soc. Edin.*, 1918-19, **39**, 143-148).—An attempt to ascertain how silver in a particular form, such as colloidal silver solutions (Bredig), can exert a bactericidal action. The impact of the larger submicroscopic particle is not the cause, whilst there is no evidence that adsorption of the silver particle takes place on the surface of the organisms. Electropositive and electronegative sols produced the same antiseptic action. The concentration of free silver ions was insufficient to explain the pharmacological action, but when the size of the particles was considered it was found that the bactericidal value may be ascribed to the ultra-microscopic particle below $15\ \mu\mu$ in diameter. J. C. D.

Vitamine Requirements of certain Yeasts. FREDA M. BACHMANN (*J. Biol. Chem.*, 1919, **39**, 235-257).—The observations of Pasteur and of Wildier on the nutritive requirements of yeast are confirmed. All the yeasts investigated grew better and fermented more readily in a medium containing some small amounts of organic material other than sugar. It is suggested that the substances which are necessary for fermentation to be carried out effectively by the yeast are of the nature of vitamins (Wildier's "bios," *La Cellule*, 1901, **18**, 313). The yeasts appear to vary considerably in their requirements for this accelerating factor. J. C. D.

Action of Radium Emanation on the Vitamines of Yeast. KANEMATSU SUGIURA and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1919, **39**, 421-433).—This investigation showed that exposure to radium emanation may cause partial destruction of the vitamins present in yeast. It is suggested that a part of the beneficial influence of radium in the treatment of malignant tumours may be dependent upon such destruction of the growth-accelerating factors. J. C. D.

The Metabolin and Antibolin of Yeast. E. VAHLEN (*Zeitsch. physiol. Chem.*, 1919, **106**, 133-178).—The author has prepared metabolin and antibolin from yeast which, although not quite identical with the similar principles previously extracted by him from the pancreas of cattle, resembled them in their main properties. Metabolin accelerates alcoholic fermentation, antibolin has the opposite effect. The principles can be transformed into each other by molecular rearrangement. An irreversible metabolin has also been prepared from yeast and potatoes. This metabolin also accelerated alcoholic fermentation and reduced the amount of sugar in the urine of diabetic patients on two occasions. S. S. Z.

The Content and the Formation of Invertase in Yeast.

H. VON EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1919, 106, 201—249).—The inversion capacity of two strains of yeast examined from time to time has been proved to be constant. The optimum temperature for invertase formation in one of these strains has been found to be 26—30°. When the temperature was raised by about 35° no invertase formation could be observed. The invertase formation is further dependent on the acidity of the medium. The maximum enzyme formation coincides with the optimum activity of the invertase. At a H-ion concentration higher than $P_H=2$ the invertase is destroyed; on the other hand, at a H-ion concentration of $P_H=6-7$ the enzyme formation is 90% of its optimum. Water at a temperature of 10° does not wash out the invertase of fresh living yeast. S. S. Z.

The Augmentation of the Catalase Activity of Yeasts.

HANS VON EULER and INGVAR LAURIN (*Zeitsch. physiol. Chem.*, 1919, 106, 312—317).—The catalase of *Saccharomyces Thermantitonus* is activated by chloroform, but not by an increase of temperature. Sunlight diminishes the action of catalase in living yeast cells, whilst X-rays have no effect on it. S. S. Z.

Ilex vomitoria as a Native Source of Caffeine.

FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, 41, 1307—1312).—Since the so-called "Paraguay Tea," which contains considerable proportions of caffeine, is derived from certain South American species of *Ilex*, the authors have examined other representatives of this genus found in the south-eastern States in order to discover possible home sources of the drug. Several species were found to contain no caffeine at all, but *Ilex vomitoria*, Aiton, appears to be worth cultivating as a source of the base. Under the name "Yaupon," the leaves were already used by the Indians for their medicinal and stimulating properties. J. C. W.

Action of Cyanamide and of Dicyanodiamide on the Development of Maize.

P. MAZÉ, VILA, and M. LEMOIGNE (*Compt. rend.*, 1919, 169, 804—807).—The results of water-culture experiments show that cyanamide at a concentration of 0.162 gram per litre prevents the germination of maize seeds, but that dicyanodiamide at this concentration is not toxic towards their germination.

Similarly, cyanamide, either with or without the presence of sodium nitrate, kills maize seedlings, whereas dicyanodiamide, in the presence of sodium nitrate, does not appreciably check the development of the plant, although with dicyanodiamide as the only source of nitrogen, the plant does not increase in weight, but yet remains alive for several months. W. G.

Presence of Formic Acid in the Stinging Hairs of the Nettle.

LEONARD DOBBIN (*Proc. Roy. Soc. Edin.*, 1918—19, 39, 137—142).—Although it is frequently stated that formic acid is present in the stinging hairs of the nettle, few attempts at a direct

proof have been made. The author collected the acid present in a very large number of hairs by compressing the leaves with filter-paper impregnated with barium carbonate. From an examination of the barium salt formed he comes to the conclusion that free formic acid does exist in the stinging hairs. J. C. D.

The Yellow Colouring Substances of Ragweed Pollen.

FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1919, 41, 1285—1289).—The pigments of ragweed pollen may be extracted by alcohol, then precipitated in fractions from an aqueous solution by means of basic lead acetate, and finally recovered from the lead precipitates in the usual way, the yield being about 0.6%. The least soluble pigment is a quercitrin glucoside, $C_{21}H_{20}O_{13}$, which fuses at 228—229° to a cherry-red oil, and thus differs from its three known isomerides, quercimeritrin, isoquercitrin, and incarnatin. Among the more soluble glucosides is one which yields isorhamnetin on hydrolysis, and this seems to be predominant. J. C. W.

Soil-sorption. E. RAMANN and A. SPENGLER (*Landw. Versuchs-Stat.*, 1918, 92, 127—146).—The interchange of bases occurring in mixed solutions containing two different bases has been studied by means of a permutite of moderately constant composition prepared in the wet way. The replacement of bases taking place when such a hydrated aluminium alkali silicate is treated with neutral potassium, ammonium, calcium, and sodium salts has the character of a chemical exchange, no signs of physical adsorption being detectable. The interchanges are by equivalents, that of potassium and ammonium following the law of mass action; the curves expressing the ratios of the ions in solution and those of the bases in the silicates are coincident. In solutions containing sodium and calcium salts the interchange of bases corresponds predominantly with the ratio of the ions in the solution, but preponderance of the calcium or sodium salts results in divergences dependent on a second factor of unknown nature. Potassium and ammonium are mutually replaceable, and displace sodium and calcium completely from the silicate, whereas the displacement of potassium and ammonium by sodium and calcium is incomplete. The ratios between the bases in the solutions and in the silicates have different values. Bases present in small proportions in the solutions are combined by the silicate in amounts greater than those corresponding with such proportions. Within wide limits, the absolute concentrations of the salts in the solution are without appreciable influence on the composition of the silicate, this being the case even with mixtures of calcium salts with those of the univalent metals. T. H. P.

Solubility of Calcium Carbonate of Different Origins and Degrees of Fineness in Water containing Carbon Dioxide in Relation to Soil and Plants.

G. HAGER and J. KERN (*J. Landw.*, 1916, 64, 325—342).—The degree of fineness of calcium carbonate influences considerably its solubility and especially its velocity of dissolution in water containing carbon dioxide,

The less prolonged the action and the greater the proportion of carbon dioxide in the water, the more marked are the differences observed with carbonates of different finenesses. The increased rapidity of dissolution, as well as the more effective distribution obtainable, probably causes the superior action on soil and plants of the more finely ground carbonate. T. H. P.

Determination of the Efficacy of the Soil Feeding Stuff, Phosphoric Acid and Potash, by Culture Experiments, and Determination of their Relative Solubility by Acids. O. LEMMERMANN, A. EINECKE, and L. FRESSENIUS (*Landw. Versuchs-Stat.*, 1916, **89**, 81—195).—A large number of pot experiments have been carried out with soils of different types, analyses of the soils especially as regards the relative solubilities of the phosphates and potassium compounds being also made. Determinations of such solubilities furnish in most cases a means of expressing the physiological efficiency of these fertilising substances. In the case of the phosphates, the best of the various solvents tried for determining the relative solubility proves to be 1% citric acid solution, and the soil may be extracted by dropping the solvent through it or by shaking it with the solvent. For potash, on the other hand, this solvent is too weak, and satisfactory results have been obtained by the use of 10% hydrochloric acid. In these determinations allowance must be made for the physical characters of the soil. The common assumption that the potassium compounds of the better soils are more difficultly soluble than those of the lighter ones is not supported by the results obtained; such assumption applies more in the case of the phosphates, this being perhaps attributable to the higher clay- and iron-contents of the better soils. The degree to which plants are able to utilise the phosphoric acid appears to increase with the poverty of the soil in phosphates. T. H. P.

Comparison of Two Fertilisers according to Mitscherlich's Law of the Minimum. MARYAN GORSKI (*Landw. Versuchs-Stat.*, 1919, **93**, 113—120).—Results obtained in fertilising experiments with increasing proportions of ammonium sulphate and sodium nitrate agree well with Mitscherlich's mathematical expression (A., 1911, ii, 760). It is shown that equality of the efficiency factors (*Wirkungsfaktoren*) for corn- and straw-yields necessitates constancy of the ratio, corn-yield:straw-yield, for different minimum factors. Calculation of the ratio between the efficiency factors for ammonium sulphate and sodium nitrate gives values which remain almost unchanged, no matter whether the efficiency factors of the corn-yield or those of the straw-yield are employed in the calculation. T. H. P.

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